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# Pyrolysis liquids and gases as alternative fuels in internal combustion engines – A review

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ABSTRACT

Liquids and gases produced through biomass pyrolysis have potential as renewable fuels to replace fossil fuels in conventional internal combustion engines. This review compares the properties of pyrolysis fuels, produced from a variety of feedstocks and using different pyrolysis techniques, against those of fossil fuels. High acidity, the presence of solid particles, high water content, high viscosity, storage and thermal instability, and low energy content are typical characteristics of pyrolysis liquids. A survey of combustion, performance and exhaust emission results from the use of pyrolysis liquids (both crude and up-graded) in compression ignition engines is presented. With only a few exceptions, most authors have reported difficulties associated with the adverse properties of pyrolysis liquids, including: corrosion and clogging of the injectors, long ignition delay and short combustion duration, difficulty in engine start-up, unstable operation, coking of the piston and cylinders and subsequent engine seizure. Pyrolysis gas can be used more readily, either in spark ignition or compression ignition engines; however, $NO_x$ reduction techniques are desirable. Various approaches to improve the properties of pyrolysis liquids are discussed and a comparison of the properties of up-graded vs. crude pyrolysis liquid is included. Further developments in up-gradation techniques, such as hydrocracking and bio-refinery approaches, could lead to the production of green diesel and green gasoline. Modifications required to engines for use with pyrolysis liquids, for example in the fuel supply and injection systems, are discussed. Storage stability and economic issues are also reviewed. Our study presents recent progress and important R&D areas for successful future use of pyrolysis fuels in internal combustion engines.



**Contents**



*Abbreviations:* BHP, brake horse power; BSEC, brake specific energy consumption; BSFC, brake specific fuel consumption; CA, Crank angle; CCHP, combined cooling, heating and power; CHP, combined heat and power; CI, compression ignition; DI, direct injection; FT, Fisher Tropsch; GHG, greenhouse gas; HC, hydrocarbon; HHV, higher heating value; IC, internal combustion; ID, ignition delay; IDI, indirect injection; IEA, international energy agency; IGCC, integrated gasification combined cycle; IMEP, indicated mean effective pressure; IOP, injector opening pressure; LHV, lower heating value; LtL, liquid to liquid; NG, natural gas; PG, pyrolysis gas; PL, pyrolysis liquid; SI, spark ignition; SMD, sauter mean diameter

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## 1. Introduction

Demand for energy is increasing due to population growth, technological progress and urbanisation. By 2100, worldwide energy demand is forecast to be five times greater than today [1,2]. We are also seeing a continual upward trend in energy prices. Government agencies and researchers are pursuing different options to fill the impending energy gap caused by increasing demand per capita, population growth, and the need to curb greenhouse gas (GHG) emissions from conventional energy sources. Among these options, biomass is unique in that it is carbon-based and provides fuels comparable to fossil fuels [3]. The use of biomass resources for energy production has already become very significant: currently biomass provides approximately 13% of world primary energy supply and more than 75% of global renewable energy [4,5]. Indeed it is estimated that bio-energy could contribute 25–33% of global energy supply by 2050 [4]. A recent report of the World Energy Council anticipates that the current expansion will continue for several decades [6]. Continued adoption of biomass will require efficient conversion routes and avoidance of competition with food and fibre [7,8].

Pyrolysis can convert biomass from a variety of sources – including agricultural and forestry residues – into liquid, solid and gaseous forms. All three output fractions have potential as fuels (either directly or after up-gradation) in various types of prime mover for transport, power generation, combined heat and power (CHP) or combined cooling heat and power (CCHP). The pyrolysis liquid (PL) is promising for use in both internal and external combustion engines, especially in internal combustion (IC) engines of the compression ignition (CI) type. The solid char is useful for heating, co-firing in coal plant, and as soil fertiliser and conditioner whereby it also provides some sequestration of atmospheric carbon. Char can also be used to produce syngas via gasification techniques [2]. The pyrolysis gas (PG) can be used in gas-fired boilers, gas turbines, spark ignition (SI) engines or dual-fuel engines. Recent reports have highlighted the opportunities to produce sustainable IC engine fuels from biomass pyrolysis [9,10]. Moreover, the UK's Carbon Trust has identified biomass pyrolysis as an interesting option to provide future transport fuels [11].

Internal combustion engines, especially CI engines, are used extensively worldwide for a variety of energy services such as transport, shipping, fishing boats, irrigation, power generation, CHP and CCHP. Most likely, they will remain popular for decades due to their high efficiency (both at full and part load) and variations in scale (from very small to very large), high power to weight ratio, low capital investment and operating costs, and fuel flexibility [12]. In 2005, the total estimated world GHG emission was 44 153 $MtCO_2$ eq. of which 66.5% was associated with energy services. The share of transportation, electricity and heat was 39.2% alone (of total emission) and 59% (of total energy-related emission) [13], with mostly IC engines (including gas turbines) and steam turbines serving as prime movers. Therefore a very large reduction in GHG emissions is possible by substitution of fossil fuels destined for IC engines with renewable alternatives such as fuels from biomass pyrolysis.

Though there have been several reviews of pyrolysis conversion techniques, parameters and products variations [14–20], relatively few have been focussed on the applications of pyrolysis fuels [21,22]. Chiaramontia et al. [22] reviewed the use of fast PL in both internal and external combustion engines for power generation, but did not cover the use of PG in IC engines. Biomass pyrolysis and its applications are still in the early stages of development [8,23]. To accelerate progress, it is important to consolidate and disseminate the outcomes of cutting-edge research. The aim of this review is therefore to present the current status and future R&D prospects of PL and PG as alternative fuels in IC engines, for the benefit of researchers involved in production and up-gradation of pyrolysis fuels. This study will also interest those involved in engine testing and development including engine and component manufacturers. The specific objectives are to (i) outline the main pyrolysis techniques and reactor types used to produce these fuels; (ii) review the properties of PL in comparison to standard fossil diesel; (iii) review the technical experience relating to CI engines running on crude and up-graded PL in comparison to standard diesel; (iv) review the technical feasibility of PG use in SI (and dual fuelled) engines; and (v) review the PL up-gradation techniques and assess the up-graded properties of the PL in comparison to crude PL. Modifications to the IC engines for use with pyrolysis fuels will also be discussed.

## 2. Pyrolysis techniques, products and operating variables

This section outlines the main pyrolysis techniques and reactor types that may be used to provide fuels for IC engines. For more in-depth reviews of pyrolysis process selection and optimisation, the reader is referred elsewhere [16,18,19,24–29].

### 2.1. Pyrolysis techniques and reactor types

Through the pyrolysis process, renewable biomass resource is converted to liquid, solid and gaseous fractions by heating of the biomass in the absence of air or oxygen. During pyrolysis, biomass vaporises, cracks and is condensed inside a reactor. The solid fraction is mainly char (which consists of fixed carbon), volatile material and ash (the inorganic component). The liquid fraction consists of hydrophilic organics, water and tars. The water may be a product of the pyrolysis process or it may simply be carried over from moisture contained in the feedstock. Pyrolysis liquid appears either as single aqueous phase or phase-separated [18,30]. The gaseous fraction consists of $CO_2$, CO, $H_2O$, $CH_4$, $H_2$, $C_6H_6$ and $C_2H_n$ gases in varying proportions.

There are two main pyrolysis techniques: slow and fast. Slow pyrolysis has been used for many centuries in traditional charcoal making but can also be carried out using modern reactors. This technique is characterised by slow heating rates, relatively long

residence times of solid and vapour, and usually a lower reaction temperature than fast pyrolysis. On the other hand, fast pyrolysis is characterised by high heating rates and short residence times. Fast pyrolysis generally requires the feedstock to be supplied as fine particles; and the reactor design must facilitate rapid removal of the hot vapours from the presence of the hot solids. In fast pyrolysis, liquid fuel (PL, also called bio-oil) condenses from the vapours and aerosols; the process also yields non-condensable gases of medium calorific value. The yield of PL decreases at high temperature and with longer residence time [16]. In fast pyrolysis, 50 – 75% (wt) of the feedstock is converted into PL [31]. Typical feed particle sizes for slow and fast pyrolysis are 5–50 mm and $<1$ mm respectively [32].

Other pyrolysis techniques include intermediate pyrolysis and flash pyrolysis. In intermediate pyrolysis, reaction occurs at controlled heating rates thus avoiding tar formation. Interestingly, the size and shape of the feed particles are less critical than in fast pyrolysis, which allows a wider variety of biomass feedstock. Whereas the low temperature of slow pyrolysis produces mainly char, intermediate pyrolysis operates in a medium temperature (450 – 550 °C) regime and with high heating rates to produce condensable vapours and aerosols. Hot gas filtration may be used to produce PL with low solids content [33,34]. Flash pyrolysis occurs with very fast heating rates of $\geq 1000$ °C/s and uses even shorter solid residence times ($<0.5$ s) than fast pyrolysis. The typical operating temperature for flash pyrolysis is 800 – 1000 °C and the biomass is supplied in the form of dust [32]. This process gives a similar product distribution as fast pyrolysis.

Table 1 illustrates that a higher amount of PL can be produced through fast, intermediate and flash pyrolysis; whereas slow pyrolysis produces a higher amount of the solid fuel (char). The most significant difference among the pyrolysis techniques is the residence time of the solid phase, which varies from ms to days. Different types of reactors used for pyrolysis include the bubbling fluidised bed, circulating fluidised bed, rotating cone, ablative reactor, vacuum pyrolysis reactor, entrained flow reactor,

**Table 1**
Pyrolysis techniques, process parameters and product yields (% wt) – wood pyrolysis [17, 24, 35].

| Technique | Temp. (°C) | Residence time | Liquid (%) | Char (%) | Gas (%) |
|---|---|---|---|---|---|
| Fast pyrolysis | 500 | Short hot vapour residence time ~1 s | 75 | 12 | 13 |
| Intermediate pyrolysis | 500 | Hot vapour residence time: 10–30 s | 50 | 25 | 25 |
| Slow-Torrefaction | 290 | Solids residence time: 30 min | – | 82 | 18 |
| Slow-Carbonisation | 400 | Very long vapour residence time: hours–days | 30 | 35 | 35 |
| Flash pyrolysis | 400 | Short solid residence time: $<0.5$ s | 65 | 24 | 10 |

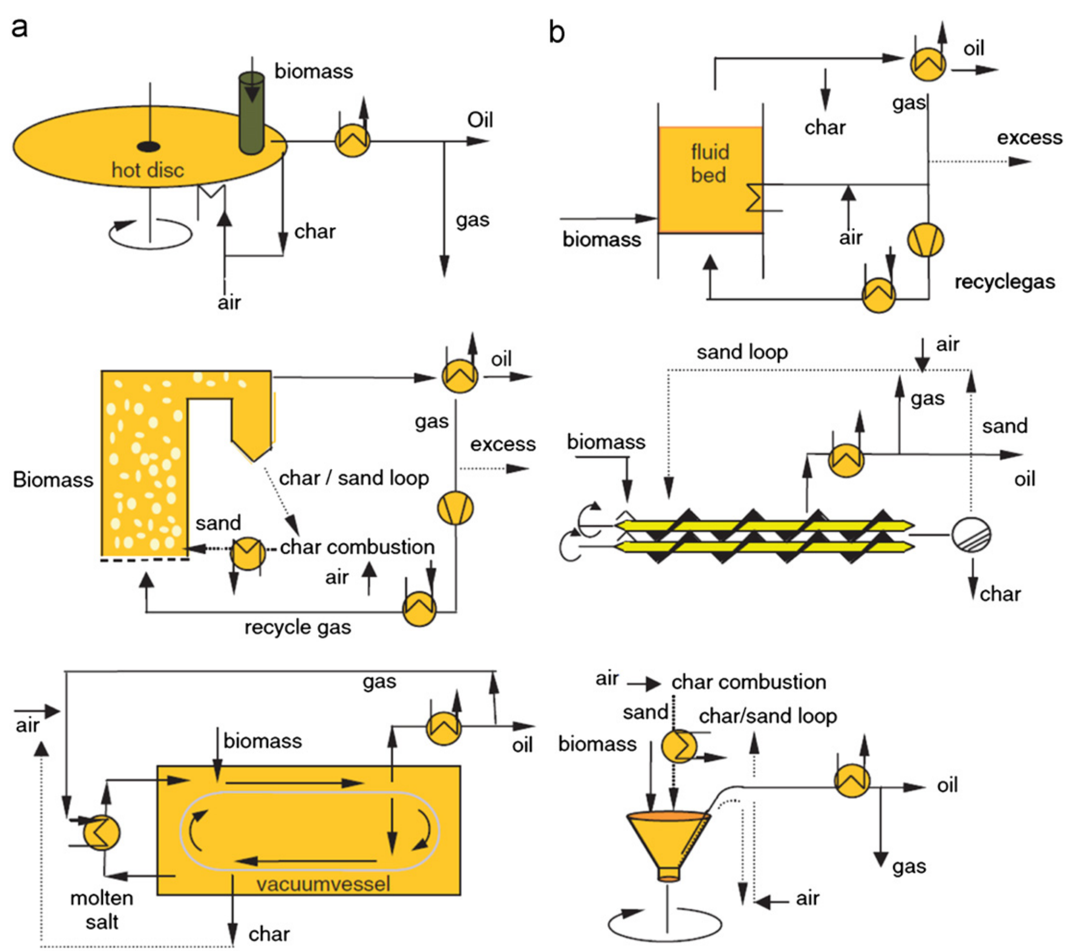



**Fig. 1.** Schematic diagram of reactors used for biomass pyrolysis [20]. (a) ablative, circulating fluidised bed and vacuum; (b) bubbling fluidised bed, auger and rotating cone.

wire mesh reactor, and auger (twin screw) reactor. The configuration and operation principles of some of these are shown in Fig. 1. The fluidised bed is the most widely used class of reactor [2,20]. Fig. 2 illustrates the fluidised bed-based fast pyrolysis process and potential uses of the PL.

### 2.2. Products and operating variables

The products (yields, properties and composition) of pyrolysis are dependent on the operating variables, biomass feedstock type, pyrolysis process and reactor design. Operating parameters such as reaction temperature, residence time, inert gas flow rate and particle size affects the quantity and quality of PL [27,38–42]. For example, Tsai et al. [39] investigated the effect of operating parameters on the product yields and composition of the fast pyrolysis of rice husk carried in a fixed-bed tubular reactor. They observed that (i) when the temperature increased from 400 °C to 500 °C (at heating rate 200 °C/min and residence time of 1 min), PL yield increased from 10% to 35%, (ii) no significant variation in the product yields occurred when heating rates increased from 100 to 500 °C/min, (iii) when the residence time increased from 1 to 2 min (at reaction temperature of 500 °C) PL yield increased from 36% to 41% and from 28% to 42%, at heating rates of 200 °C/min and 400 °C/min respectively. Optimal yield was obtained at −10° condensation temperature among temperatures of 0, −10 and −20 °C. The heating value of PL was found to be maximum (18.2 MJ/kg) at a reaction temperature of 500 °C, heating rate of 400 °C/min and residence time of 1 min [39]. In another study using fast pyrolysis, Park et al. [41] investigated the effects of reaction temperature on the pyrolysis of agricultural residues and found that the optimum temperature for maximum PL yield was about 500 °C for garlic stem and about 480 °C for pepper stem.

Inert gas flow rate and particle size plays an important role on pyrolysis products. Inert gas used in the pyrolysis process takes away the volatilities from the reactor and helps to avoid secondary reactions and re-polymerisation. Short residence time and high inert gas flow lead to minimum secondary decomposition [40]. Investigations into the fast pyrolysis of linseed showed that the PL yield was maximum at reaction temperature of 550 °C, at a heating rate of 300 °C/min and inert gas flow rate of 100 $cm^3$/min [40]. Particle size affects the heat transfer: larger particles give incomplete reaction [41] and the resulting PL yield will be less. Thus, PL yield from fast pyrolysis of lignocellulosic biomass decreased from 56.9% to 51.3% when the particle size was increased from 0.5 to 2.5 mm [42].

In a study using slow pyrolysis, Ozbay et al. [43] varied the reaction temperature during pyrolysis of cottonseed cake in a

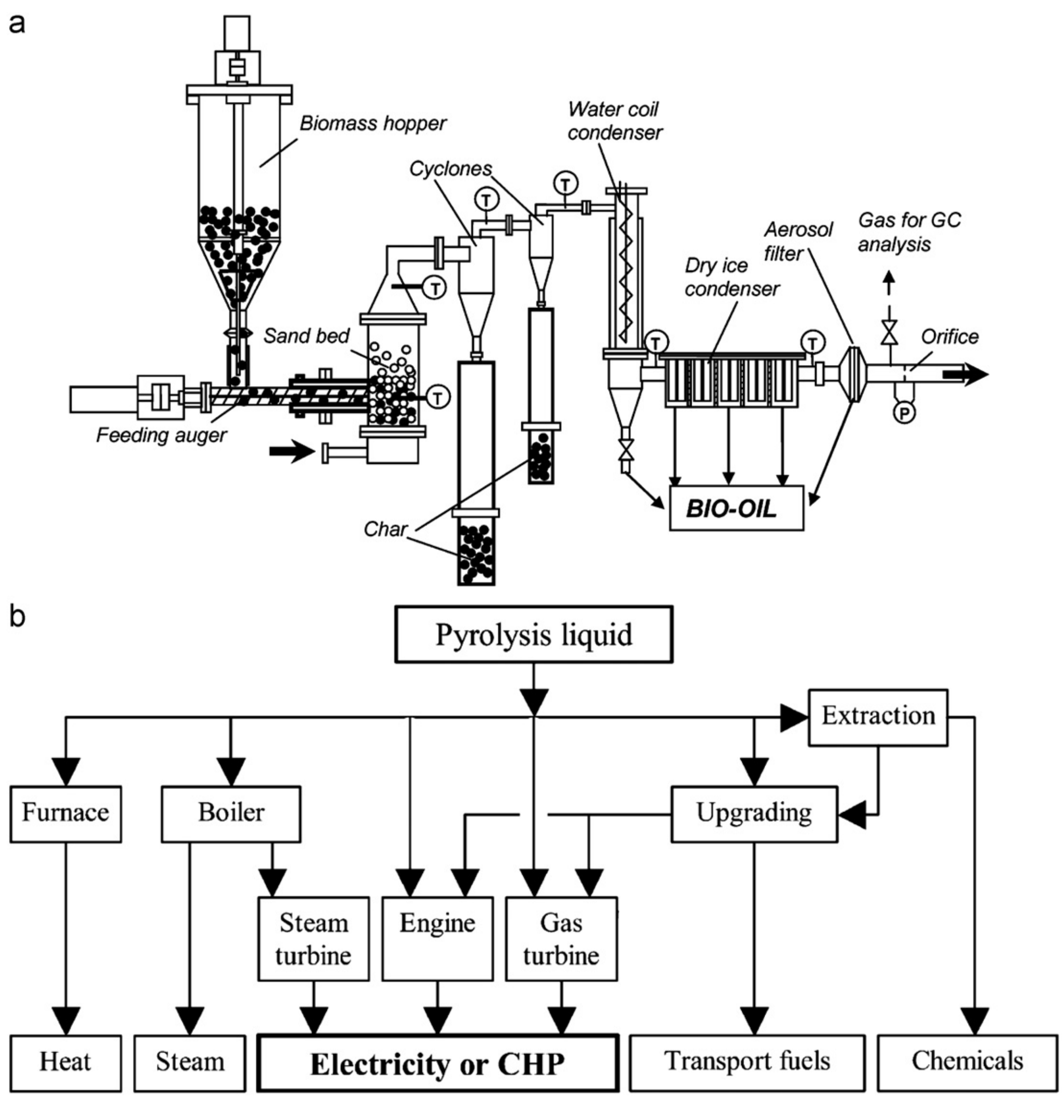



**Fig. 2.** (a) Schematic diagram of the fluidised bed fast pyrolysis process [36] and (b) potential application of the fast pyrolysis liquid [37].

tubular reactor. They reported an increase in PL output with temperature of up to 550 °C followed by a decrease above 650 °C [43]. In contrast, Bridgwater et al. [27] found PL yield from mallee through slow pyrolysis remained almost constant when the temperature increased from 420 °C to 600 °C. Yields clearly depend on the biomass feedstock type as shown by Putun et al. [44] who pyrolysed *Euphorbia rigida*, sunflower and hazelnut shell at three different temperatures of 400, 500 and 700 °C. They obtained the highest amount of PL at around 500 °C for all three feedstock. Other investigations of slow pyrolysis using rapeseed [45] and safflower seed [46] illustrated that PL yield peaked at 550 °C and was higher with smaller particles [45,46].

Cellulose and hemicellulose components in biomass feed rapidly decompose over narrower temperature ranges compared to lignin component which decomposes over a wider temperature range [25]. Demirbas [47] studied the relationship between the feedstock composition and pyrolysis product yields and found that the yield of PL and its calorific value increase with lignin composition in the feed.

As with PL, the composition of the PG depends on various factors such as biomass feedstock and operating temperatures [19, 48–50]. Luo et al. [48] researched on the fast pyrolysis of *Pterocarpus indicus* to study the effect of temperature on product distribution and composition. Their study illustrated that PL output decreased above 755 °C, and $CH_4$ and CO components in the PG product increased with temperature, whereas the amount of $CO_2$ decreased with temperature. Kucuk and Demirbas [19] pyrolysed municipal refuse samples to investigate the influence of the reaction temperature on the composition of the PG and observed that the hydrocarbon (HC) content in the PG decreased from 32.5% to 20.9% (vol.) when the temperature was increased from 134 °C to 410 °C, which illustrates that the higher amount of HC is achieved in the PG at lower reaction temperatures.

## 3. Composition and properties of pyrolysis liquids and gases

In Section 2 we discuss pyrolysis techniques, products and operating variables. Now we review the properties of the resulting pyrolysis liquids and gases as opposed to fossil fuels to assess the preliminary feasibility of PL use in IC engines.

### 3.1. Pyrolysis liquid

Pyrolysis liquid is a complex emulsion of water and oxygenated hydrocarbons. In crude condition and at room temperature it is a dark-brown free flowing liquid. Following hot-vapour filtration it may acquire a more translucent red-brown appearance due to the removal of char. Sometimes high nitrogen content in the PL can give it a dark green tinge [51]. Generally, PL consists of two phases: a lighter aqueous phase of low molecular weight and a non-aqueous phase of heavier molecules. The heavier part is mainly aromatics and is in principle suitable as a substitute for fossil diesel fuel. The lighter part mainly consists of chemicals such as acetic acid and hydroxyacetone, which emit an unpleasant odour and lower the flash point.

Both organic and inorganic compounds are found in PL. The chemical composition of typical wood-derived fast pyrolysis liquid is $C_2H_5O_2$ [12]. Pyrolysis liquid contains a mixture of carbon, hydrogen, oxygen, acids, alcohols, aldehydes, esters, ketones, sugars, phenols, guaiacols, syringols, furans, lignin derived phenols, and extractible terpene with multi-functional groups [14]. Typical PL from fast pyrolysis is made up of the following constituents: 20 – 25% water, 25 – 30% water insoluble pyrolytic lignin, 5 – 12% organic acids, 5 – 10% non-polar hydrocarbons, 5 – 10% anhydrosugars and 10 – 25% other oxygenated compounds [52]. Compounds in PL vary and depend greatly on the pyrolysis technique, biomass type and other operating parameters as reported by Khor et al. [53], Park et al. [41] and Bridgwater et al. [54]; for example, fast PL contains more aldehydes and ketones than slow PL. The presence of aldehydes and ketones make PLs especially hydrophilic and highly hydrated; consequently it is difficult to eliminate water from them [14]. Phenols and ester compounds are more present in slow PL than in fast PL [53,54]. Esters may help PL to mix with biodiesel.

A comparative picture of the physical and chemical properties of the PL (produced from a wide variety of biomass feedstocks and using different pyrolysis techniques), fossil diesel, biodiesel and neat plant oil has been compiled and given in Table 2. The viscosity, density, surface tension and acidity values of PL's are much higher than for the corresponding fossil diesel fuel. Waste tyre yielded liquid of superior properties compared to typical feedstocks [56,58]; unlike most PL, it was miscible with fossil diesel. The properties in Table 2 and their likely effects in IC engines are discussed below [5, 12, 14–17, 47, 51, 52, 65, 67–73]:

(a) *Water content*: Water in PL comes from chemical reactions and directly from the biomass feed. Water content can be measured by Karl–Fischer titration and may be as high as 15 – 30% (wt) depending on the moisture content of the feedstock. The water reduces the heating value of the PL, but can also be beneficial in that it helps to reduce the viscosity and to increase the fluidity. Water content also lowers the flame temperature, which helps to reduce the $NO_x$ emissions. For CI engines application, high water content is not favourable for ignition because it affects local temperature and vaporisation rates. Water in the fuel also contributes to an increase in the ignition delay (ID) period. Moreover, high water content may cause erosion problem in the injectors and fuel supply systems. Water in PL is homogeneously dissolved and difficult to eliminate by drying.
(b) *Viscosity*: Viscosity measures the internal resistance to flow. For PL it is very high compared to fossil diesel fuel and varies widely in the range of 25 – 1000 cSt. Viscosity is an important parameter in terms of the design and operation of the fuel injection system and fuel supply systems to the engine. Viscosity is reduced if the PL has less water insoluble compounds. Addition of alcohols helps to reduce the viscosity. It was reported that an addition of 5% methanol (wt) in hardwood PL decreases the viscosity by 35%. Viscosity is temperature dependent and can be reduced through preheating. The chemical structure of the PL can change with time leading to larger molecules. Hence, the viscosity of PL may change through polymerisation and condensation reactions.
(c) *Acidity and solids content*: Pyrolysis liquid contains carboxylic acids, such as acidic and formic acids. These lead to low pH values, typically in the range 2 – 4. Acidity causes corrosion and tends to increase with temperature. Consequently, materials selection to handle and use PL may be problematic. Acceptable materials include 300 series stainless steels, high density polyethylene (HDPE) and fluorinated HDPE.
Normally there are some solids present in PL such as fine char particles and ash. This leads to coking in the engine injectors and erosion. The solids content can be measured as insoluble residue in a methanol-dichloromethane mixture and is typically in the range 0.1 – 1%. Presence of solids also leads to high particulate matter (PM) emissions. PL does not contain excessive amounts of alkali or heavy metals. Hot corrosion occurs in the combustion system when alkali metals and other compounds interact.
(d) *Heating value*: The heating value of a fuel depends on its chemical composition and density. Fuels having only carbon

**Table 2**
Comparative properties of pyrolysis liquid, fossil diesel, biodiesel and neat plant oil.

| Biomass/fuel name | Pyrolysis technique/parameters | HHV (MJ/kg) | LHV (MJ/kg) | Viscosity (cSt) at 40 °C | Water (% wt) | Density (kg/m$^3$) | Flash point ($^0$C) | pH value | Ash (% wt) | Carbon res (% wt) | Stoic *A*/*F* ratio | C (% wt) | H (% wt) | N (% wt) | O (% wt) | S (% wt) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Rice straw | Fast pyrolysis – fluidised bed reactor | – | – | 71 at 50 °C | | 1.009 | 69 | 4.07 | 0.007 | – | – | – | – | – | – | – | [55] |
| Wood | Fast pyrolysis | 18.0 | | 833.33 | 25 | 1.20 | | 2.5 | Trace | – | – | 57 | 6 | Trace | 37 | | [17] |
| Waste tyre | Vacuum pyrolysis of passenger car tires | 43.7 | – | 9.7 at 50 °C, 3.2 at 100 °C | 0.3 | 0.950 | 28 | – | Trace | 1.3 | – | 86.5 | 10.8 | 0.5 | 2.2 | 0.8 | [56] |
| Waste tyre | Vacuum pyrolysis of waste tyres | – | 38.0 | 3.77 | – | 0.924 at 15 °C | 43 | – | 0.72 | 0.31 | – | 83.48 | 13.12 | 0.22 | 2.46 | 0.72 | [57,58] |
| Corncob | Slow pyrolysis, distillation temp. range from 110 to 220 °C. | 36.4 | – | 9.1 | – | 1.006 | 94 | – | – | – | 9.6 | 73.7 | 11.4 | – | 10 | – | [59] |
| | Slow pyrolysis, distillation temp. range over 220 °C. | 37.1 | – | 14.82 | – | 1.01 | 108 | – | – | – | 9.8 | 76.3 | 11.67 | – | 10.1 | – | |
| Pine charcoal | Slow pyrolysis Traditional klin | – | 35.6 | – | 1.22 | 1.031 at 20 °C | 49 | – | – | – | 12 | 80 | 9.7 | < 0.005 | 10.3 | – | [60] |
| Wood | NREL Ablative pyrolysis | – | 17.0 | – | 16.9 | 1.220 | – | – | – | – | 6.45 | 58.25 | 7.40 | 1.53 | 47.4 | – | [61] |
| Wood | ENSYN Rapid thermal process | – | 16.3 | – | 26.3 | – | – | – | – | – | 5.62 | 57.95 | 7.23 | 1.64 | 42.7 | – | [61] |
| Canadian oak (ENEL1) | Fast pyrolysis. Transported bed reactor | 18.21 | 16.94 | 570 at 25 °C | 23.1 | 1.230 at 20 °C | – | 3.2 | – | – | – | 44.06 | 5.79 | 0.08 | 48.68 | < 0.01 | [62] |
| Beech wood (ENEL 2) | Produced by ENEL, same plant as ENEL1 | 15.87 | 14.58 | 8.412 at 25 °C | 45.1 | 1.165 at 20 °C | – | 3.0 | – | – | – | 34.96 | 5.94 | 0.11 | 58.70 | – | |
| California pine (DYNA 1001) | Produced by Dynamotive. Bubbling fluid reactor | 18.16 | 16.80 | 39.32 at 25 °C | 31.1 | 1.175 at 20 °C | – | 2.6 | – | – | – | 43.52 | 6.31 | 0.07 | 50.07 | – | |
| BTG pine wood | Produced by BTG, rotating cone reactor | 17.46 | 16.09 | 17.91 at 25 °C | 34.4 | 1.189 at 20 °C | – | 2.9 | – | – | – | 44.08 | 6.18 | 0.09 | 49.64 | – | |
| Rice husk | Fast pyrolysis, temp. range: 420–550 °C. Electrical heater, fluidised bed reactor | – | 17.42 | 128 | 25.2 | 1.190 | – | 2.8 | – | – | – | 41.7 | 7.7 | 0.3 | 50.3 | 0.2 | [49] |
| Sawdust | | – | 18.2 | 240 | 19 | 1.300 | – | 2.1 | – | – | – | 53.5 | 6.4 | 0.2 | 40.2 | 0.1 | |
| Mixture: (1:1) by wt | | – | 17.4 | 156 | 20.7 | 1.255 | – | 2.6 | – | – | – | 46.5 | 7.3 | 0.2 | 49.8 | 0.1 | |
| Pine | ENSYN fast pyrolysis VTT. Finland | 18.2 | 16.6 | 23.1 at 50 °C | 21.3 | 1.230 | – | – | – | – | – | 44.9 | 7.4 | < 0.1 | – | | [63] |
| Fischer Tropsch diesel | Fischer Tropsch synthesis fuel. | 44 | 34.3 | 3.57 at 20 °C | – | 0.78 | 72 | – | – | – | – | – | – | – | 0.1 | – | [64] |
| Plant oil | Pure plant oil (Jatropha oil) | 39.77 | – | 49.9 at 27 °C | – | 0.918 | 240 | – | – | 0.22–0.44 | – | – | – | – | – | – | [65] |
| Commercial diesel | Fossil | 45.80 | – | 3–8 | – | 0.83 | 79 | ~7 | 0.00 | – | 14.82 | 86.6 | 13.2 | < 0.005 | 0 | – | [53,59,61] |
| Biodiesel (B100) | Produced from used rapeseed oil | – | 36.7 | 9.48 at 30 °C | 0.11 | 0.895 | 192 | – | – | – | – | 77.1 | 13.8 | – | 9 | 0.002 | [66] |
| Heavy fuel oil | Fossil | 40 | – | > 1000 at 20 °C, 175 at 50 °C | 0.04 | 1.01 | – | – | 0.05 | 12 | – | – | – | – | – | 2.3 | [12] |
| Light fuel oil | Fossil | 42.4 | – | 14 at 20 °C, 6 at 50 °C | 0.02 | 0.87 | – | – | 0.01 | 0.02 | – | – | – | – | – | 0.18 | [12] |

and hydrogen tend to have higher heating values. Because PL has oxygen and other compounds, its heating value is only about 40 – 50% that of diesel. However, heating values based on stoichiometric mixtures are almost the same for PL as for fossil diesel, though the stoichiometric air/fuel ratio differs. A relatively low stoichiometric ratio offsets the lower heating value of the PL. The LHV based on the stoichiometric mixture for typical PL is 2.28 MJ/kg, compared to 2.79 MJ/kg for the fossil diesel; and the stoichiometric air/fuel ratios for PL and diesel fuel are 6.45 and 14.5 respectively. Here it is worth mentioning that the heating value of the PL increases if biomass with high lignin content is pyrolysed.

(e) *Density*: The density of PL is generally higher than that of water and fossil diesel fuel: it lies in the range of 1.15–1.25 kg/m$^3$. Density gives an indication of the specific energy content and also the ignition quality. The literature reports a relation between density and $NO_x$ emission; the higher the density the more $NO_x$ emitted. In comparison to fossil diesel fuel, the energy content of PL is around 60% on volume basis and 40% on weight basis.

(f) *Carbon, hydrogen, nitrogen, oxygen and sulphur content*: The carbon content in PL is generally less than in fossil diesel fuel; it is around 40 – 60% for fast PL, and around 70 – 80% for slow PL. Hydrogen content is around 6–8% for fast PL and around 10 – 12% for slow PL. In fast PL, oxygen content is in the range 35 – 50% (wt), which is much higher than in fossil fuel and biodiesel; correspondingly PL has lower energy content (almost 50% of the fossil fuels). High oxygen content also leads to difficulties in mixing with fossil/hydrocarbon fuels. Oxygen content in PL produced from slow pyrolysis process is only around 10%. Oxygen tends to make PL unstable. Levels of S and N in PL are very low. For example, *S* and N content in PL produced from sawdust using the fast pyrolysis technique is 0.1% (wt) and 0.2% respectively.

(g) *Ash content*: Ash is the inorganic materials present in PL and this value leads to estimate the amount of abrasive materials present in the fuel. Presence of ash can cause erosion, corrosion and kicking problems in the engine; alkali metal compounds in the ash aggravate erosion. Sodium, potassium and vanadium are responsible for high temperature corrosion and deposition. Particle size distribution of the ash is often critical for the engine injection system.

(h) *Surface tension*: The surface tension of PL is higher than fossil diesel fuel. Surface tension at 20 °C is 29.3 mN/m for fossil diesel fuel as compared to 34.7 and 40 mN/m for NREL M2-10 and ENSYN RTP 15TPD pyrolysis liquid. This property affects the Sauter Mean Diameter (SMD) and hence the combustion behaviour in engines.

(i) *Carbon residue*: Carbon residue indicates the tendency to form coke or deposits during combustion. It is normally measured using the Conradson carbon residue tester. Asphalt present in the fossil fuel leads to carbon deposit formation in the combustion chamber. Carbon residue in PL is 10–70% higher than fossil diesel fuel due to the presence of solids and other compounds in PL.

(j) *Flash point*: Flash point is defined as the minimum temperature at which the fuel produces enough vapour to ignite. Flash point of the PL could be either higher or lower than fossil diesel depending on the biomass feedstock. Fuel with flash point of 90 °C or greater is considered as non-hazardous under US department of transport regulations. In general, PL has low flash point temperature and extra care should be taken during storage and transportation of the PL. In contrast, most biodiesel and pure plant oils have higher flash point temperatures.

(k) *Cetane number*: This is an important characteristic of a CI engine fuel and represents the ignition quality. This number indicates the ignition delay i.e. the duration between the start of injection and the start of combustion (or ignition); the higher the cetane number, the shorter is the ignition delay. Measured values on the cetane numbers of the PL are not available in literature. The estimated value (using empirical formulae) of the cetane number of wood-derived PL blend (blended with 12% ethyl alcohol) has been reported as 30, whereas cetane numbers of fossil diesel and typical biodiesel are around 47 and 45 respectively. This illustrates the low quality ignition properties of PL.

(l) *Miscibility*: Water can be added to the PL, but there is a limit (around 35%) to how much water PL can take before phase separation starts. Pyrolysis liquid is miscible with polar solvents such as methanol, acetone, etc. In general, PL is not miscible with fossil derived fuels.

(m) *Distillation*: Pyrolysis liquid cannot be vaporised fully once recovered from the vapour phase. Pyrolysis liquid starts boiling at around 100 °C and, due to its complex composition, has a wide range of boiling points. If PL is heated to 100 °C or more to try to remove water or distil lighter fractions, it produces a solid residue of around 50% (wt) of the original liquid and some distillate containing volatile organic compounds and water. In other words, PL is chemically unstable, and its instability increases with temperature.

### 3.2. Pyrolysis gas

In addition to condensable vapours, pyrolysis produces non-condensable gases of low molecular weight. If secondary cracking of the vapours is used, further non-condensables are obtained generally having greater heating value compared to the primary gas [74]. The LHV of the natural gas (NG) is around ~37 MJ/m$^3$; and for typical PG this value is in the range of 5.5–7.0 MJ/m$^3$. The main components of the PG are $N_2$, $H_2$, CO, $CO_2$ and $CH_4$. Other components present may include $H_2$ and $C_2$-chain gases [2]. High inert gas ($N_2$) and low hydrocarbon content in the PG caused poor LHVs of the PGs.

The PG composition changes depending on the biomass type and reactor parameters [41,49,75,76]. Using a fluidised bed reactor with electric heating, feedstocks of rice husk, sawdust and mixture of and the two were pyrolysed (by fast pyrolysis) to produce PL, PG and char [49]. The variation in the composition of PG can be seen from Table 3. In another study, non-catalytic and catalytic pyrolysis of corn cobs and corn stalks were performed in a fixed bed reactor to investigate the pyrolysis products (solid, gas and liquid) in two different reactor configurations [75]. The results illustrated that LHVs of the PG (calculated based on the molar ratio of CO, $H_2$, $CH_4$ and hydrocarbons $C_2H_4$, $C_2H_6$ present) and gas composition is dependent on the reactor temperatures – for example, LHV of the cob PG was ~11.5 MJ/m$^3$ at 600 °C and this was increased by around 22% when the reactor temperature increased to 700 °C. Similar results were reported for

**Table 3**
Composition of the un-condensable gases vs. biomass feedstocks [49].

| Gas from rice husk | | Gas from sawdust | | Gas from mixture (1:1) | |
|---|---|---|---|---|---|
| Composition | wt% | Composition | wt% | Composition | wt% |
| $N_2$ | 88 | $N_2$ | 86 | $N_2$ | 87 |
| $H_2$ | 0.01 | $H_2$ | 0.02 | $H_2$ | 0.02 |
| CO | 2.24 | CO | 3.40 | CO | 2.58 |
| $CO_2$ | 7.62 | $CO_2$ | 9.20 | $CO_2$ | 8.42 |
| $CH_4$ | 0.54 | $CH_4$ | 0.63 | $CH_4$ | 0.57 |
| $C_2H_4$ | 0.27 | $C_2H_4$ | 0.30 | $C_2H_4$ | 0.28 |

**Table 4**
(a) Unmodified/crude pyrolysis liquid use in CI engines (standard or modified engine).

| Biomass feedstock and pyrolysis process | Fuel preparation and fuel supply systems modifications | Engine specification, modification of the engine components/parts | Results and experiences | Ref. |
|---|---|---|---|---|
| Hard wood PL produced by ENSYN Rapid Thermal Process, and Poplar PL produced by NREL Vortex Ablative Process. | 40 μm stainless steel mesh and 10 μm paper based filter were used in the fuel supply system. Fuel switch over system: fossil diesel, nitrate-enriched ethanol to clean and then PL. Injector return was collected separately and not mixed with the fuel supply. Four hole injector, IOP −250 bar. | Ricardo Hydra Mark four single cylinders, DI engine. Four hole injector, IOP −250 bar. Lubrizol 9520 A additive was used (0.1% vol) for lubricity properties of the ethanol. Di-ethylhexylnitrate was added (15% vol) to ensure good ignition quality of the ethanol. Lubrizol additive was also used with the PL. Kistler pressure transducer and amplifier was used to measure cylinder pressure. | Reported smooth engine operation. Long ID with PL operation observed. Air preheating to 55 °C was required to ignite the PL. Achieved similar thermal efficiency (indicated) of 36% for both PL and diesel. Rate of pressure rise is 30–70% lower than fossil diesel. Engine sustained less than 3 h/day with PL. Fuel pump required overhauling, injector nozzle required replacement, build-up of the carbon deposits in the combustion chamber occurred including valves, cylinder and piston. | [67] |
| PL produced from waste tyres. Vacuum pyrolysis technique. | PL is miscible with fossil diesel. Direct blending of PL with fossil diesel fuel at different proportions – 20%, 40%, 60% and 80%. Modified fuel supply system was adapted. | Kirlosker single cylinder diesel engine. Rated power 4.4 kW at 1500 rpm. No modifications to the engine carried out. | Engine was stable up to 70% PL blend. No injector clogging occurred. For 70% PL blend and at full load, thermal efficiency was 11% Lower, CO emission is almost double, and $NO_x$ emission as 30% higher than fossil diesel. ID is higher by 4° CA than fossil diesel for the same blend. Peak pressure, rate of pressure rise and rate of heat release are higher compared to diesel operation. 20% and 40% PL blend (with fossil diesel) produced better performance. | [57,58] |
| Hard wood flash PL produced by Ensyn Technologies Inc. (Canada). VTT and Wartsilla collaboration. | Unmodified PL was used. Ignition improver was used: ignition improver 2 from Ethyl Corporation and N-Cet from ICI. PL blend preparation, fuels supply system and operation sequences has been discussed in Section 4.1 of the study. | Tests carried out at VTT, Finland. Single cylinder Peter AVB diesel engine, bore/stroke: 80/110 mm, DI, displacement: 553 $cm^3$, comp. ratio: 15.3:1, rated power 4.8 kW at 2000 rpm, injection timing: 24° BTDC. Injection timing not varied. AVL INDICOM used to measure various combustion parameters. | Stable operation not achieved. Injector clogged quickly and performance changed. Injection duration, ignition delay and heat release results discussed in details in Section 4.1. At 50% load, PL with 5% ignition improver produced similar $NO_x$ and HC emission, and double CO emission than fossil diesel; whereas 5% increase in the smoke was observed. | [12,77] |
| Hard wood – flash pyrolysis, and PL produced from straw. VTT and WARTSILLA collaboration. | Unmodified PL was used. Cetane/ignition improver was added to PL. fuel supply system modified – twin injection. Flushing done with ethanol. Starting with diesel and then ethanol and then PL, flushing done | Valmet 420 modified pilot injection high speed 4-cylinder turbocharged CI engine. Max. Power: 64 kW, at 1500 rpm, DI, Bore/stroke: 320/120 mm. Injection timing: 17° BTDC. Cylinder head was modified for twin injection. | Stable operation achieved with twin/pilot injection. Severe corrosion of the standard injector reported. PL burns rapidly once combustion started. Later, Wartsilla developed a corrosion resistant injector and tested, which, also experienced clogging. | [12,22,77] |
| Rapeseed pyrolysis liquid – Intermediate pyrolysis. | Unmodified PL was used. Conducted two test: blend of 15% ethanol and 85% PL, and 100% PL. | Schnell 250 kW diesel engine. Tested in one cylinder out of six cylinders. Designed separate air intake and fuel supply/injection system for test cylinder. Reference fuel was used in other five cylinders. | Blended PL with 15% ethanol tested for 30 min – no damage of the injector detected. For 100% PL – severe injector corrosion was observed only after 3 h of operation. Detailed results not available. Cylinder temperature was 10% higher for both tests, compared to rape methyl ester. Detailed results not available. | [78] |
| 01. Canada PL – Flash pyrolysis of eucalyptus. 02, Modified oil – produced from wood in Spain | Crude PL was used. PL was preheated to 90 °C. Modified PL was produced by filtration, water and light acids vacuum- extraction and addition of 53.8% ethyl alcohol. | LOMBARDINI 6LD 435/B1 engine, bore/stroke: 86/75 mm, compression ratio: 18, rated power: 4.93 kW (6.71 bar), Injection pressure: 220 bar. Ethyl alcohol was used to warm up the engine and to flush out the fuel supply and injector systems. | Self-ignition of crude PL not achieved even preheated to 90 °C, 12% alcohol addition to Canada oil helped ignition. Results discussed in Section 4.1. Injection pump and injector needle were clogged after a few minutes of operation, Found thick carbonaceous deposits inside combustion chamber and exhaust valve. Fuel leaked to crankcase; crankpin bearing seized in less than 1 h of operation. | [72] |
| Pyrolysis tar from pine using traditional kiln – slow PL | Stable blends containing 20% and 40% PL with fossil diesel were prepared. Viscosity value was reduced by preheating before injection. | VAMO D3900K diesel engine. 4-stroke, 4-cylinders. Compression ratio: 16.1. Max. power: 57 kW at 2500 rpm. Engine was tested at four different loads. SMD of fuel was measured for the blends to optimise the blend injection temperature. | Stable engine operation achieved. At full load, brake thermal efficiencies were 2% and 4% lower that of diesel operation for 20% and 40% blends respectively. Higher density tar compensated heating value which resulted similar heat release like | [60] |

**Table 4** (*continued*)

| Biomass feedstock and pyrolysis process | Fuel preparation and fuel supply systems modifications | Engine specification, modification of the engine components/parts | Results and experiences | Ref. |
|---|---|---|---|---|
| | | | diesel. Other results discussed in Section 4.1. | |
| Corncob tar from gasification industry, PL was extracted from tar by distillation: PL1-between 110 and 220 °C and PL2-above 220 °C. | Stable blends of PL and fossil diesel produced. PL1 and PL2 were mixed separately and total of 18 blends were prepared. Due to high viscosity and low volatility only two blends containing 10% PL1 and 10% PL2 were tested. | FZD engine test bed. ZH100B 4-cylinders, 4-stroke engine, air cooled DI engine; rated power: 11.03 kW at 2200 rpm. Analyser NHA-500 and photometer NHT-1 (Fushan Nanhua instrument Co.) were used to analyse the exhaust gas and smoke. No modification of the fuel or air supply system carried out. | Stable engine operation observed. At part load conditions, 11.7% and 6.6% lower fuel consumption were observed for PL1 and PL2 blends (10% PL plus 90% diesel) operation respectively as compared to fossil diesel fuel, and this is almost similar at full load. At full load, reduced amount of CO and $CO_2$ emissions were reported for both blends than fossil diesel – discussed in Section 4.1. | [59] |
| Waste wood flash pyrolysis liquid, produced by Ensyn Technologies Inc. VTT and WARTSILLA collaboration- engine tests carried out at WARTSILLA | PL was filtered using 10–20 μm filter. Cetane improver was added to PL to improve the ignition quality. Ignition was through pilot injection. Pilot diesel injection in one cylinder and rest fuel is PL, reference/diesel fuel in other cylinders. Pilot diesel quantity was between 3.2% and 4.6% of maximum diesel flow in other cylinder. | Wartsilla Vasa 18V32, compression ratio:12, 410 kW/cyl at full load and at 750 rpm. Injection timing: 17° BTDC. Designed and manufactured twin design nozzle (two needle) using corrosion resistive material, injection timing and duration in test cylinder was varied for PL. PL nozzle: 9 × dia 0.78 × 150°; Pilot diesel nozzle: 5 × dia 0.30 × 144°. Electronically controlled pressure amplifier system has been developed in order to avoid camshaft's modification. | Full cylinder power achieved through pilot diesel injection. Comparable thermal efficiencies were obtained for the PL, it is 44.9% at full load in test cylinder. Rate of cylinder pressure rise curve is not as smooth like diesel, which may be an indication of minor knocking. Combustion duration is shorter. Lower $NO_x$ and CO emissions and higher HC emissions were observed in test cylinder. Corrosion of standard pump plunger was reported after 4 h of operation, but no corrosion/ erosion of the nozzle assembly (new material) reported except some carbon deposits on the surface. | [79] |
| Pyrolysis liquid produced from mixture of waste frying oil and castor oil (mixed at 1:1 ratio). | Stable blends of PL-diesel were prepared without using the emulsifier – using 10%, 30% and 50% PL. No modification to the fuel supply systems or injectors carried out. | Kirlosker TV1, Rated capacity: 7.37 kW at 1500 rpm, bore/stroke: 80/110, compression ratio: 17.5, injection timing: 27° CA, IOP: 200 bar. No modification of the engine or components. AVL gas analyser was used to analyse exhaust gas. | Stable engine operation reported for all blends. At full load, the fuel consumption (wt) decreased by 23% and 12% respectively for 10% and 50% PL blends; exhaust temperature of PL blends is around 3% higher than 100% fossil diesel. $NO_x$ emissions for all three blends and at full load are around 26–32% higher that fossil diesel operation. HC emission is higher at all load condition. $NO_x$ and HC emissions decrease as % of PL increases in blends. CO emission is either same or higher at low load condition, but at full load CO emission decreased considerably: for example, CO emission of 10% and 50% PL blends are 0.05% and 0.02% respectively, against 0.06% for fossil diesel. | [80] |
| Pine wood fast pyrolysis liquid; produced by BTG, Netherland. | PL was blended with ethanol, butanol and biodiesel. Pure PL, PL-ethanol, PL-biodiesel and PL-butanol-biodiesel blends were tested in the diesel engine. Specific blend consisting of 60% PL, 30% butanol and 10% biodiesel (by weight) was tested in the engine. The compression ratio and fuel supply components of the engine were modified. Three fuel supply tanks (diesel, ethanol, PL) were used. | JIANG DONG single cylinder 20 kWe (at 2200 rpm) diesel engine. Engine was modified – compression ratios: 17.6 (original) and 22.4 (after modification). Stainless steel injector and fuel pump was used. Inlet air was preheated for combustion of PL. Compression ratio was increased by modifying the piston. Investigated the influence of compression ratios, injection timing, addition of cetane improver and air inlet temperatures. Engine was first started with diesel, then switched to ethanol and after that finally switched to PL. | Engine was operated successfully with PL (and blends) for 40 h at low loads (3–4 kWe). Compared to fossil diesel operation, CO emission was increased and $NO_x$ emission was decreased when operated with PL (or PL blends). Change in ignition timing did not improve engine performance during PL fuelled operation. Peak cylinder temperature was lower than diesel operation. Inlet air heated to 100–120 °C allowed stable combustion of PL (and blends) when engine compression ratio was 17.6; but this was reduced by 40 °C when compression ratio was increased to 22.4. Addition of ignition improver did not improve PL fuelled engine operation. | [81] |
| Tyre pyrolysis liquid produced from waste automobile tyres using vacuum pyrolysis technique. | Pure tyre pyrolysis liquid mixed with ignition improver was tested in the diesel engine. Ignition improver (diethyl ether) was added in the air intake manifold and mixed with the air intake. Diethyl ether was added at | Kirloskar single cylinder water-cooled DI type diesel engine. Compression ratio: 17.5, rated power: 3.7 kW at 1500 rpm. Injection pressure and timing: 180 bar, 14° BTDC. No modification of the engine was | Stable engine operation was observed when ignition improver was used. Higher flow rate of diethyl ether (130–170 g/h) produced better engine emissions. $NO_x$ emission was decreased by 5% than diesel | [82] |

**Table 4** (*continued* )

| Biomass feedstock and pyrolysis process | Fuel preparation and fuel supply systems modifications | Engine specification, modification of the engine components/parts | Results and experiences | Ref. |
|---|---|---|---|---|
| | three flow rates (65 g/h, 130 g/h and 170 g/h) to investigate the engine performance and emissions. No emulsifier was used. | carried out. Engine was first started with diesel and then switched to tyre PL-diethyl ether operation. | operation. At full engine load HC, CO and smoke levels were up by 2%, 4.5% and 38% respectively than diesel. Peak cylinder pressure was higher by about 3 bar and ignition delay was longer by 2.8° CA. At full load, thermal efficiency was decreased by 2.5% than diesel operation. | |
| Pyrolysis oil was produced from de-inking sludge waste (obtained from local paper industry) through intermediate pyrolysis at Aston University, Birmingham, UK. | Stable blends of PL-biodiesel (20% and 30% PL) were produced without using any emulsifier. No ignition improver was used. Standard injector and fuel pump were used. Additional fuel filters were used in the fuel supply system. | Lister Petter water cooled three cylinders IDI type diesel engine. Rated power: 9.9 kW at 1500 rpm. Compression ratio: 22, Injection timing: 20° BTDC. No modification of the engine was carried out. Engine was first started with diesel and then switched to PL-biodiesel blend operation. Kistler pressure sensors and Kibox were used for combustion analysis. | Full engine power was achieved with both 20% and 30% PL blends. Engine operation was stable with 20% PL operation, but indicated minor knocking in the case of 30% PL blend operation. Compared to diesel operation (at full engine load) and for both blends: fuel consumption was 6% higher on volume basis, thermal efficiencies were similar, peak cylinder pressure was up by 5–6%, combustion duration was decreased by 12%. Start of combustion was delayed for PL-biodiesel blends, $CO_2$ emission was increased by 4% and $NO_x$ emission was decreased by 6–12% as compared to diesel operation. | [83] |

(b) Modified/up-graded pyrolysis liquid use in CI engines (in standard or modified engine).

| Biomass feedstock and pyrolysis process | Pyrolysis liquid up-gradation techniques and fuel supply systems modifications | Engine specification, modification of the engine components/parts | Results and experiences | Ref. |
|---|---|---|---|---|
| PL derived from pine sawdust (60–80 mesh, 2.5 kg/h). Fast pyrolysis at 450–550 °C, fluidized-bed reactor, preheated $N_2$ (300 °C, 3 m3/h) was used as fluidizing gas. | Stable emulsions of aqueous fraction of PL and fossil diesel were prepared in ultrasonic condition. Two emulsifiers were prepared, by mixing surfactants span-80, Tween-80, Tween-20, TritonX-100, and n-octanol at ratio of 72:9:9:0:10 (mix1) and 63:9:9:9:10 (mix2) (% wt). 3% mix1 emulsifier proved high emulsification performance. | Single cylinder, naturally aspirated, 4-stroke, air-cooled, DI diesel engine. Rated power: 2 kW at 3000 rpm (Chongqing Camel Power Machinery Co., Ltd, PRC) Engine was tested at a constant injection timing of 17° CA BTDC at different loads from 200 W to 1800 W with an increment of 200 W and at 3000 rpm. PL, Fossil diesel and mix1 emulsifier was blended at a ratio of 10:90:3 for engine testing. | Compared the results with diesel operation, exhaust temperature was lower at low load condition and almost similar when load exceeds around 1.4 kW. At 1.6 kW load, $NO_x$ emission was ~7 times lower and CO emission was ~3 times higher, $CO_2$ emission increased by 14.3%, $O_2$ emission decreased by 20%, and $SO_2$ emissions increased sharply to 60 ppm from ~3 ppm at 1.2 kW load. Corrosion and clogging of the injector occurred. | [84] |
| Wood-derived PL – Fast pyrolysis | PL was emulsified with fossil diesel using emulsifier. Stable emulsions were prepared at 5%, 25%, 50%, 75% (vol) PL content. Used three fuel tanks: diesel, emulsion and bleed. Modified fuel supply system designed and implemented (see Section 4.3 for details). | Lombardinin 6LD400, DI (5.4 kWe, 3000 rpm) air cooled (four holes in injector), IEE-1, DI (5.3 kWe, 2450 rpm) water cooled (five holes in injector), IEE-2 (5.9 kWe at 850 rpm) water cooled (one hole in injector) and ORMROD (250 kWe, 750 rpm) water cooled (six holes in injector) engines. Stainless steel nozzle was manufactured. | Twenty three tests were conducted both with conventional and stainless steel nozzle. Severe corrosion of the standard injector channels observed in Lombardini engine along with rapid damage of the fuel pump and injector holes. Engine was tested with up to 25% PL-diesel blend: results discussed in see Section 4.3. Operation with stainless steel nozzle led no wear. | [62,85] |
| PL (derived from various biomass feedstock). | Emulsifier was developed at University of Florence, Italy. Emulsifier details not available. Emulsion with fossil diesel (10–70% PL) was produced, which were stable over a year. | PL emulsions tested in small diesel engines at Pasquali Macchine Agricole (Italy) and Kassel University (Germany). Also, tested in a 250 kWe multi-cylinder diesel engine at Ormrod Diesels Ltd. (UK). | Demonstrated successful short term combustion in the diesel engines. No injector problem observed. Detailed results not available – study concluded that further work needed to verify long term operation of PL emulsions. | [86,87] |
| – | PL was emulsified with fossil diesel at different ratios using Emulsifier – details not available. | Tractor engine was selected for testing (technical details not available). | Short duration tests of the tractor engine in the field powered with emulsions were successful. Detail results not found. | [88] |
| 01.Pine wood PL produced at VTT (Finland) using the ENSYN fast pyrolysis process. 02.Pine wood PL produced at Dynamotive (Canada) using the RTI fast pyrolysis process. | Diglyme (diethylene glycol dimethyl ether, cetane number: 112–130) was used to prepare blends due to its high cetane number and low gaseous emission properties. Stable blends of PL and Diglyme were prepared at a ratio of 15.1%, 30%, 44.1% and 56.8% PL (wt). Two different micro-emulsions were also prepared using emulsifier. No preheating of the | Ruggerini RP 170 single cylinder DI engine, bore: 100 mm, stroke: 95 mm, compression ratio: 18, rated power: 11 kW, 3000 rpm, swirl supported combustion chamber. Fuel injector: four holes (dia 0.28 mm), cone angle 160°. IOP was set at 210 bar. Injection timing varied. No air (or fuel) preheating. Return from the injector was not reintroduced into | Stable engine operation was observed up to an hour for the PL and Diglyme blend with PL content of up to 44.1% (using PL of VTT). For 44.1% PL blend: fuel consumption is ~2.5 times higher, HC and $NO_x$ emissions are 75% and 67% lower, CO emission is around 48% higher, $O_2$ emission is ~8% lower than fossil diesel. Rate of cylinder pressure rise and heat release is | [63] |

**Table 4** (*continued* )

| Biomass feedstock and pyrolysis process | Fuel preparation and fuel supply systems modifications | Engine specification, modification of the engine components/parts | Results and experiences | Ref. |
|---|---|---|---|---|
| | blend. Engine started and stopped with diesel. | the fuel supply system. After every run the injector was dismantled and inspected. Tests were conducted at 1250 rpm and IMEP of 4.3 bar. | higher than fossil diesel. ID increased as the amount of PL increases in the blend. Micro-emulsions with diesel produced unexpected combustion behaviour with sharp peak in the heat release rate. For 30% VTT-diesel emulsion $NO_x$ emission was 46% lower, and for 30% dynamotive-diesel emulsion, it is ~27% higher than fossil diesel. No major problems occurred in the engine or its components including injectors. | |
| PL derived from Eucalyptus (Fast pyrolysis). PL's obtained from other sources were also tested. | Engine tests carried out by Ormrod Diesels Limited. PL was used in three modified cylinders (out of six cylinders). Quantity of fossil diesel injected was 5% and rest was PL. Methanol was added in doses during intermittent periods to enable the switch over from fossil diesel to PL. | Modified 250 kWe, 700 rpm dual injection engine. Two fuel pumps per cylinder: one for PL and other for pilot diesel fuel. Cylinder head was modified for dual injection. Designed and built the PL injection and fuel supply systems. Polypropylene and/or stainless steel was used for the PL fuel supply lines. Fuel changeover system was implemented. | Total 300 h of experience gained on eucalyptus PL. Overall efficiency on PL was 33.8% (as dual fuel mode) as compared to 34.1% on methanol and 36% on diesel. Lower $NO_x$ and $SO_x$ emissions, CO emission higher. PL would produce the same power as diesel fuel but needed approximately 40% (vol.) more PL. Other PL's produced from various feedstock tried but stable operation of the engine not achieved (detail not available). | [89] |
| PL (detail not found) | Fuel supply system modified. Dual injection of PL: 95% PL as main fuel and 5% diesel. This 95% PL was used in stages – 1st stage: 80% PL and 20% methanol mixture, 2nd stage: 10% methanol and 90% PL mixture, 3rd stage: 100% PL was used in the main injector. | 250 kWe Mirrlees Blackstone six cylinder medium speed diesel engine. Naturally aspirated. PL was tested in one cylinder out of six cylinders. Engine was completely dismantled and rebuilt for modification to dual fuelled type. | No specific measurements were taken. Illustrated that PL can be used in the modified diesel engine in dual fuel mode with 5% pilot diesel fuel and 95% PL. The engine ceased when the pilot diesel fuel was shut off completely. The un-burnt PL formed a black lacquer inside the combustion chamber which was removed with methanol and parts were reused. | [90] |
| PL derived from beech wood. Fast pyrolysis (BTG, the Netherlands). PL up-gradation and engine tests were carried out at the University of Groningen, The Netherlands. | PL was hydrotreated using catalysts in a 5 l batch autoclave: mild hydro treated oil (HDO) at 320–340 °C and 200–250 bar and 2nd stage HDO (mild HDO as feed) at 340 °C and 200 bar were produced. Engine started with diesel, switched to ethanol: methanol: water (85:5:10) mixture, and subsequently to the up-graded PL. | Single cylinder, Hatz 1D31S engine, bore/stroke: 86/65 mm, swept volume: 377 $cm^3$, comp ratio: 21, rated speed: 3000 rpm, rated power: 5 kW. Injection timing: 20°CA BTDC. Intake air was preheated for ignition. Inlet air temperature for the mild and 2nd stage HDO was set to 170 °C and 95 °C respectively. | Engine operation not successful when crude PL was used; heavy smoke generated and engine stopped by itself. Smooth engine operation reported with HDO oil and operated for 1.5 h in total when only preheated intake air was used. Exhaust emission, corrosion and erosion of the injectors were discussed in Section 4.1. | [91,92] |

corn stalks PG. Also it was observed that in the case of cob PG and at 500 °C temperature, LHV of the PG produced through catalytic pyrolysis is around 9% higher than non-catalytic one. Furthermore, heating value of the PG can vary widely on biomass feedstock, for example, HHVs of the PG produced from garlic stem and pepper stem through fast pyrolysis process were 8.86 MJ/kg and 4.77 MJ/kg respectively [41].

## 4. Pyrolysis liquid combustion in compression ignition engines

The PL properties reviewed in Section 3 – such as low heat content, high viscosity, high solid content, high acidity, and low re-polymerisation temperature – suggest that problems may arise in CI engines. In this section we will review the overall experience actually gained in this respect and make reference to studies of specific interest.

As with other types of alternative fuel, engine testing with PL typically involves assessment of performance and emissions through measurement of parameters such as brake power, brake thermal efficiency, brake specific fuel consumption (BSFC), brake specific energy consumption (BSEC), indicated mean effective pressure (IMEP), peak cylinder pressure, heat release (peak and rate), combustion duration, injection duration, injection pressure, ID, exhaust temperature, smoke opacity, particulate in exhaust gas and the composition of exhaust gases ($CO_2$, $NO_x$, HC, $O_2$, CO). These parameters are normally compared to values for standard fossil fuels. Pyrolysis liquids have been tested both in standard and in modified CI engines. A comprehensive summary of CI engine test results, operating difficulties and experiences with crude and up-graded PL respectively is presented in Table 4a and b. This summary shows that it is difficult to use crude PL in existing CI engines without up-grading (or blending) the PL or modifying the engine components. In the case of crude PL, many engine tests were not successful with some tests lasting only minutes or a few hours; but interestingly, some engine tests were successful using PL-diesel and PL-biodiesel blends (Table 4a).

Some of the common problems associated with the combustion of the crude PL in standard CI engines are (i) difficulty in starting the engine due to the poor ignition quality of PL, and subsequent unstable operation; (ii) higher fuel consumption than fossil diesel operation (in some cases it was not possible to attain full power due to the limitations of the fuel pumps and injectors capacity); (iii) higher CO emission (though $NO_x$ is typically lower than corresponding fossil diesel operation); (iv) corrosion and

erosion of the fuel supply systems and injector components; (v) particulate emissions due to solids in the PL; (vi) both injection duration and ignition delay parameters are higher for PL in comparison to fossil diesel; (vii) burning duration is lower than fossil diesel; (viii) wear of the engine body material and other components due to acidity and the solids content of PL; (ix) coking of the piston and cylinder liners, and engine seizing; (x) polymerisation of the PL, due to the change of temperature during fuel injection. On the other hand, Table 4b demonstrates that up-graded PL can successfully be used in the standard or modified CI engines.

Due to poor ignition quality, it is difficult to combust crude pyrolysis oil in CI engines. Higher ID exhibited by PL than fossil diesel operation has been reported by several researchers [12,57,58,60,61,67]. A study of particular interest is that of Solantausta et al. [12], who tested wood-derived fast pyrolysis liquid in a 4.8 kW (2000 rpm) Petter AVB single cylinder diesel engine. They used a complex test procedure comprising several stages: start and warm up with diesel fuel, switch over to ignition-enhanced ethanol, switch over to ignition-enhanced PL, 12 min running on PL, switch over to ethanol to clean the injection system, and then continued alternation between PL and ethanol. Engine and fuel injection systems were not modified but ignition improver was used at different ratios. Two different types of ignition additives were used: Diesel Improver 2 from Ethyl Corporation and N-Cet from ICI. The former was found to be immiscible with PL, whereas up to 10% (vol.) of the latter could be incorporated allowing tests to be carried out with 3%, 5% and 9% N-Cet improver. Four different types of fuels were tested: standard fossil diesel, low quality reference fuel (RF35), ethanol (ETOH) and PL. Despite the ignition improvers, stable engine operation was not achieved with PL and injectors became clogged (Table 4a). Fig. 3 shows the injection timing and ignition delay

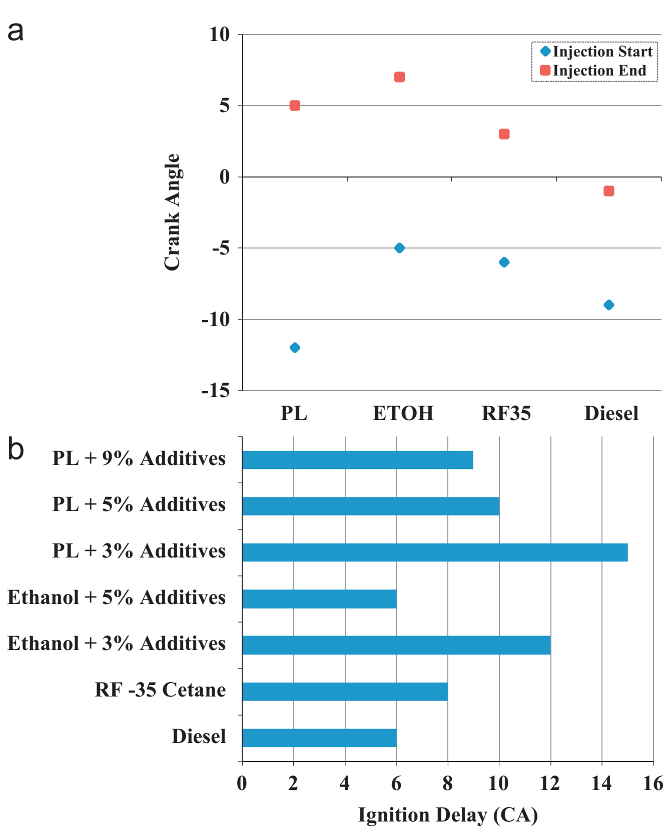



**Fig. 3.** (a) Injection timing, (b) ignition delay behaviours of wood PL and other fuels. (redrawn – data taken from Ref. [12]).

(ID) behaviour of the fuels tested. With fossil diesel injection starting at 9° BTDC, the injection duration was approximately 8° Crank Angle (CA) – see Fig. 3a. For ethanol, fuel injection started at 5° BTDC and duration was around 12° CA. Due to the high viscosity of PL, the injection was earlier at 12° BTDC and the duration was 17° CA. Ignition delay for fossil diesel was 6° CA and for poor ignition quality reference fuel it was 8° CA (Fig. 3b). For the PL (with 3% ignition improver), ID was 15° CA and ID decreased with the increase of the amount of ignition improver. The heat release diagram revealed that that the time required for 10–90% heat release was roughly 22° CA for fossil diesel and 13–17° CA for PL, demonstrating that although ID of PL is high (meaning that it is difficult to ignite) it combusts quickly after the start of combustion [12]. A number of studies have shown that the high ID of PL caused comparatively higher cylinder pressure rise and heat release rates compared to fossil diesel operation [57,58,67], which may contribute to knocking.

In their study of crude PL in a CI engine, Shihadeh and Hochgreb [67] favoured inlet air preheating to aid combustion. They tested a single cylinder Ricardo Hydra diesel engine with PL after some modifications to the fuel supply system. Another study by the same authors reported longer ID reflecting poor ignition quality of the PL [61]. In this case, ignition characteristics were compared for two different types of wood-derived flash pyrolysis liquid (produced by the ENSYN and NREL processes). It was observed that the NREL liquid exhibited considerably better ignition characteristics than the ENSYN liquid. At higher charge temperature, ID of PL's was close to fossil diesel [61]. Peak heat release of PL was lower than with fossil diesel; the NREL liquid illustrated higher heat release than the ENSYN liquid. The authors concluded that PL combustion in CI engine is primarily limited by slow chemistry and not only quality of mixing and atomisation which is the case for fossil diesel. Chemical composition, molecular weight and water content of the PL play an important role in ID [61,67]. The presence of water affects the heat of vaporisation and vaporisation rates. The NREL pyrolysis liquid had lower water content and lower molecular weight compared to ENSYN pyrolysis liquid (Table 2), which led to better ignition performance. Also, additional thermal cracking in the NREL process appears to have up-graded the fuel resulting in improved chemical and vaporisation characteristics [61].

Frigo et al. [72] tried eucalyptus wood-derived flash pyrolysis liquid in a standard diesel engine and found that the fuel would not ignite even after preheating to 90 °C; however, it did self-ignite when mixed with 12% ethyl alcohol with preheating temperature to 50 °C. These authors observed that at 3.5 bar load (at 2000 rpm), the smoke emission and fuel consumption were 42% and 3.3 times higher than fossil diesel, when the engine was operated at similar ignition timings of 5° CA BTDC. Similar ignition timing was set by varying the injection timing for each fuel. The air-fuel ratio for diesel fuel was 35 and this value dropped to 13.6 for PL blend. Peak cylinder pressure was increased by 16% relative to fossil diesel operation. Ignition delay of the PL blend was reported as 7° CA [72], a big improvement compared to 15° CA reported by Solantausta et al. [12]. The injection duration was longer, and combustion duration was shorter than fossil diesel. The injection system clogged, however, after just a few minutes of operation [72].

Although PL is not usually miscible with fossil diesel, stable blends of PL and fossil diesel have been produced and smooth operation of the engines reported [59,60,80]. Lower oxygen content in the slow pyrolysis oil helps it to mix with fossil diesel. Combustion performance results using blends of pine-derived slow PL (20% and 40%) and fossil diesel show that that peak cylinder pressure and temperature was increased by 6% and 3% respectively, when 40% blend (with diesel) of slow PL was used in

**Table 5**
Combustion performance of a slow pyrolysis pine tar and fossil diesel blends (at full engine load condition, 2000 rpm) [60].

| Fuel | Max in cylinder ressure (bar) | Max in cylinder temp. (K) | Max fuel injection pressure (bar) | Ignition delay (°CA) | Fuel injected during ID (mg) | LHV (MJ/kg) | Energy stored during ID (kJ) |
|---|---|---|---|---|---|---|---|
| Diesel (100%) | 91.4 | 2249 | 348 | 9 | 21 | 43.50 | 0.91 |
| Pine tar/diesel blend (20:80) | 92.7 | 2217 | 385 | 10 | 25 | 42.14 | 1.05 |
| Pine tar/diesel blend (40:60) | 97.0 | 2316 | 426 | 12 | 36 | 40.34 | 1.45 |

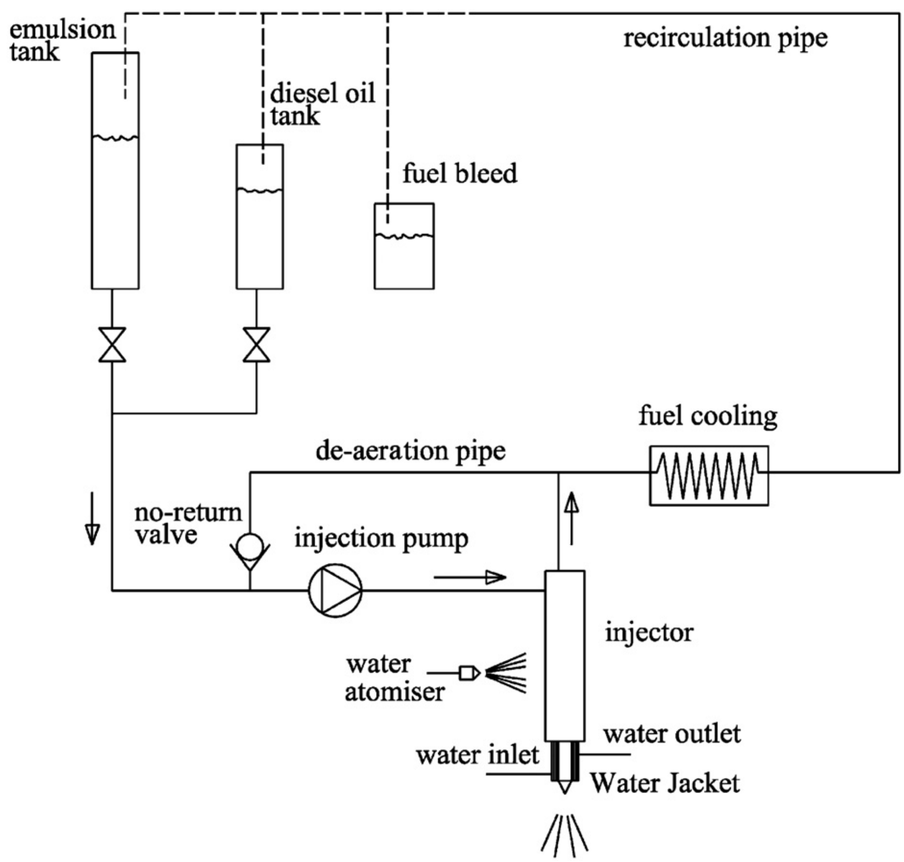



**Fig. 4.** Modified fuel supply system [85].

the engine instead of fossil diesel (Table 5). The higher fuel consumption by 71% in the case of PL blend caused increased pressure and temperature. Ignition delay was increased by 33% and peak injection pressure was increased by 22%, when the 40% PL blend was used (Table 5). Zhang and Wang [59] derived PLs through distillation at two different temperature ranges of the tar, which was a by-product of the corncob gasification plant: PL1 was produced by distillation at 110 – 220 °C; PL2 by distillation at > 220 °C. Two stable blends were prepared using 10% PL1 or PL2 plus 90% fossil diesel for engine tests. With these blends, full engine power was achieved and the engine could even run overloaded. Compared to diesel: (i) fuel consumption decreased by 11.7% (PL1 blend) and 6.6% (PL2 blend) at part load and was almost similar at full load; (ii) CO emission decreased by 19% (PL1 blend) and 43% (PL2 blend; this was attributed to the lower carbon content); (iii) $CO_2$ emission was decreased by 14% (PL1 blend) and 14% (PL2 blend) respectively. However, HC emission was slightly higher at all loads indicating some levels of incomplete combustion. Smoke levels were similar at full load condition, but lower by 20 – 40% at part loads.

Up-graded PL has been tested in CI engines. For example, a series of engine tests was carried out by Wildschut [91] at the University of Groningen using catalytically hydrotreated PL produced from beech wood by BTG in The Netherlands. Crude PL was hydroprocessed using Ru/C catalysts to produce two up-graded pyrolysis liquids: mild hydro treated oil (HDO) treated at 320–340 °C and 200–250 bar pressure and 2nd stage HDO (using the mild HDO as feed) treated at 340 °C and 200 bar. The oxygen contents in mild and 2nd stage HDO were 20.3% and 12% respectively. (Properties of hydrotreated PL will be discussed in Section 6 of this study.) Crude PL, mild HDO, 2nd stage HDO and fossil diesel were tested in a 5 kW HATZ diesel engine. Stable engine operation was achieved after preheating the intake air to 160–170 °C (mild HDO) and 60–130 °C (2nd stage HDO). Without preheating, much smoke was generated and the engine stopped after a few minutes. $NO_x$ emission was much lower than with the fossil diesel. This is due to the high water content in HDO (low combustion temperature) as explained by other researchers [93,94]. Compared to diesel operation, CO emission was higher and $CO_2$ emission was comparable for both types of HDO. Scanning Electron Microscopy (SEM) of the injector nozzle

**Table 6**
Engine test results with modified fuel supply system [85].

| Emulsion type (PL content by vol.) | Warm up time with diesel (min) | Duration of operation with emulsion (min) | After test operation with diesel (min) | Power generated (kW) | Emulsion fuel consumption (litres) | Fuel supply system modification | Injection channel diameter after test run (mm) (initial dia 0.2 mm) |
|---|---|---|---|---|---|---|---|
| 25 | 20 | 78 | 8 | 3.1 | 1.1 | Standard engine | 0.6 |
| 5 | 25 | 53 | 12 | 3.2 | 1.5 | Water atomiser | 0.25 |
| 25 | 32 | 116 | 25 | 3.2–3.3 | 4.5 | Water atomiser | 0.70 |
| 25 | 30 | 81 | 15 | 3.0–3.1 | 2.6 | Water jacket+atomiser | 0.45 |

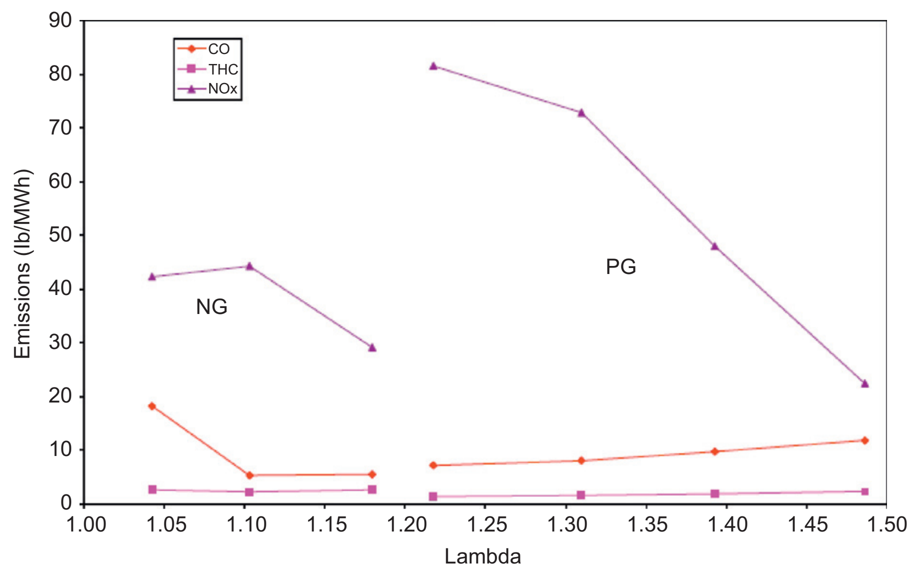



**Fig. 5.** Exhaust emissions vs. lambda values of NG/PG gas fuelled SI engine at 13 kW load [97].

after use with HDO for just a few minutes showed severe of erosion or corrosion when no preheating was used; however, with pre-heating this problem was much less severe even after 1.5 h of operation [91].

As another approach to facilitate use of CI engines with crude or up-graded PL, a number of researchers have modified the fuel supply and injection systems. In one such study, Chairamonti et al. [85] obtained improved engine performance and reduced exhaust emissions with wood derived PL-diesel emulsions. To overcome the problem of PL instability at higher temperatures, they redesigned the fuel supply system (Fig. 4) to study the effect of injector cooling. A Lombardini 5.4 $kW_e$ (3000 rpm) single cylinder and direct injection type engine was selected for this study. The injection pressure was 200 bar and the injectors were of standard type each having four injection channels (0.2 mm diameter, 0.6 mm length, 150° injection angle). Modifications allowed different cooling modes (water jacket and atomiser) of the injector to be selected (Fig. 4). Chairamonti et al. [85] found that, although the geometry of the injector channel altered (due to corrosion and erosion) when PL-diesel blends were tested in the engine, this effect was less when injector cooling was adopted (Table 6). Thus, after around 80 min of operation with 25% PL emulsion, injector channel diameter was increased to 0.45 mm with injector cooling and to 0.6 mm without cooling. The performance decreased as the amount of PL increased in the blend. At part load and for 25% PL blend [85]:

- efficiency was initially similar with and without cooling, but decreased with time more sharply without cooling. Thus after 30 min the efficiency had dropped only 14% with cooling, compared to 20% without.
- as the diameter of the nozzle increased with time, the efficiency and $NO_x$ emission decreased due to the incomplete combustion of the emulsion.
- CO emission increased with time. After 60 min of operation, CO emission with dual cooling (jacket plus spray) was almost 1.25 times higher than with single cooling (spray only). Exhaust gas temperature was lower with injector cooling than without.

Chairamonti et al. [85] also tested 25% diesel-PL emulsion in another engine having a stainless steel nozzle instead of a conventional one. In this case they used a single cylinder 5.9 $kW_e$ (850 rpm) FM II water cooled and indirect injection type engine (P.M. Diesel Ltd., India). The stainless steel (type V4A/671-1.4435) nozzle was manufactured and used with a conventional steel needle. The engine was operated for 6.5 h with no wear to the nozzle but the needle was severely damaged.

Pyrolysis liquid has also been tested using dual injection techniques in multi-cylinder engines [79,89,90]. These studies used PL as the main fuel and diesel as the pilot fuel in the test cylinder, while the remaining cylinders ran on diesel alone. Substantial modifications to the cylinder head were needed to accommodate dual injection. Though stable engine operation was achieved, corrosion and erosion of the injectors was not avoided (Table 4a and b).

## 5. Pyrolysis gas combustion in spark ignition and compression ignition engines

### 5.1. Pyrolysis gas in SI engines

Pyrolysis gas can substitute NG or producer gas in SI engines. Heating value, flame speed velocity and ignition energy are

important parameters regarding the feasibility of using such low quality gaseous fuels. Low flame velocity may lead to knocking; nonetheless, the literature has reported a similar power output of SI engines when fuelled with PG instead of NG or methane [95–99].

A series of engine tests have been reported with PG from NREL's Thermochemical Process Development Unit, where a 2-step indirect gasification process has been developed [95–97]. Pyrolysis gas, produced from mixed hardwood and softwood pellets, with heating value of 15 – 16.5 MJ/m$^3$ was tested in a 17 kW 4-cylinder standard SI engine with compression ratio of 9.4 and ignition timing of 30° BTDC [97]. The composition of the PG was $H_2$ 17.9%, CO 34.9%, $CH_4$ 15.8%, $C_2H_4$ 4.7%, $C_2H_2$ 1%, $C_2H_6$ 0.5%, $CO_2$ 17.3%, $N_2$ 6%, $H_2$/CO 0.5%. The engine was tested for over 100 h with comparisons made against standard NG operation. Similar power was achieved but the PG gave less stable engine performance. Fig. 5 illustrates the exhaust emissions of PG and NG operation. Higher emission of $NO_x$ (by a factor of nearly 2) from PG operation was attributed to the unstable ethylene and acetylene in the fuel [97]. High $H_2$ content in PG increases flame temperature thus also contributing to $NO_x$ emission [98]. On the other hand, the NREL studies showed that CO and HC emissions were comparable to NG operation. Further, experiments were successfully carried out with high $A/F$ ratio (i.e. lean burn technique) to reduce the $NO_x$ emission; but at the same time emissions of CO and THC were slightly increased (Fig. 5).

Some researchers have simulated PGs and blends of PG with NG in SI engines to investigate the performance and combustion characteristics [98,100]. Shudo et al. [98] used model PGs, to simulate the PG produced from shredder dusts of disposed vehicles, in a single cylinder SI engine running at 1000 rpm with constant volumetric efficiency of 45%. They studied the effects of heating value and composition of PG (LHV was 5.02 – 8.79 MJ/m$^3$) and used optical analysis to investigate the influence of the inert gas (present in PG) on flame propagation. Thus Shudo et al. [98] proved that model PGs with heating value as low as 5.02 MJ/m$^3$

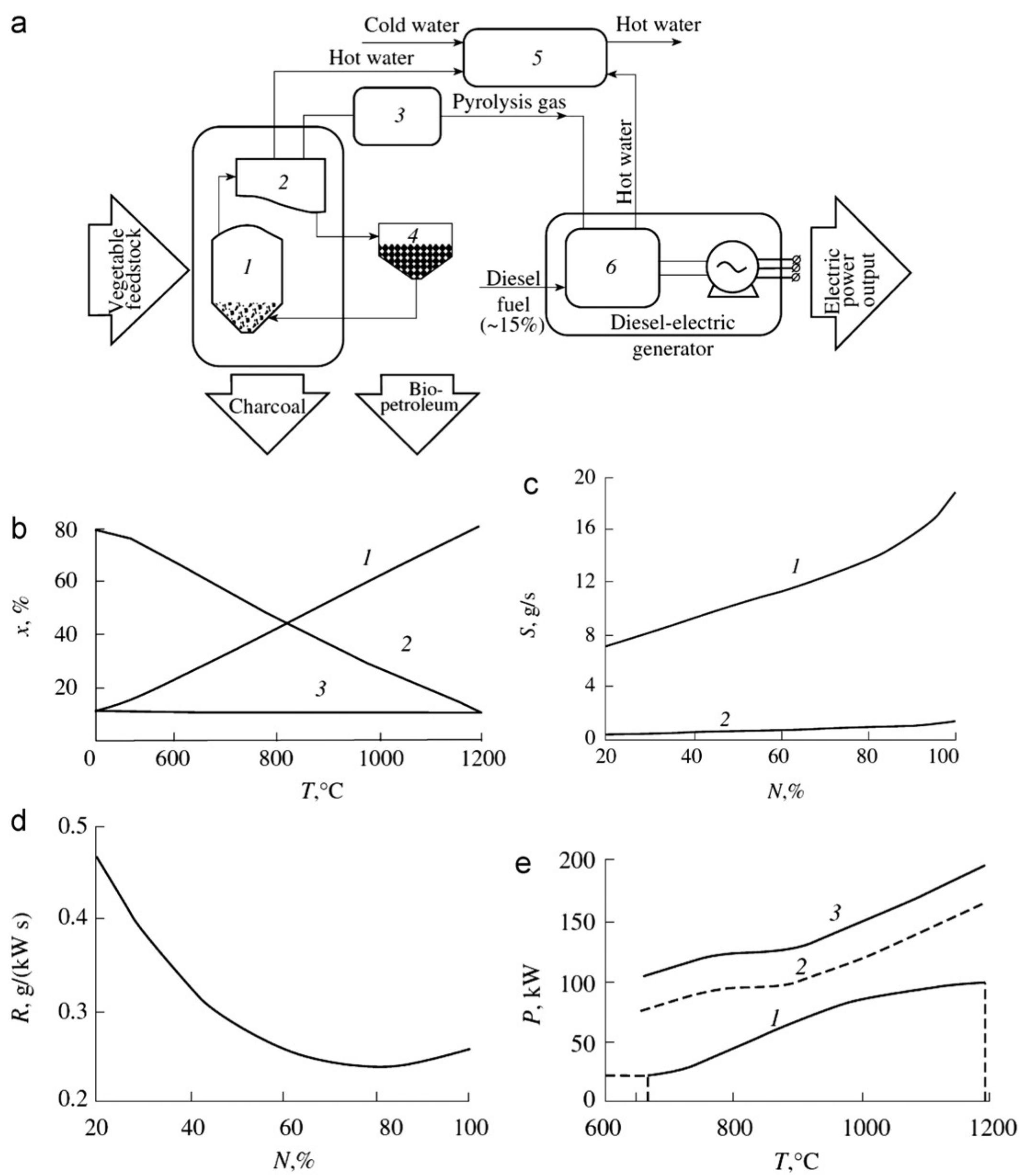



**Fig. 6.** Pyrolysis gas use in a CI engine (a) reactor and engine components 1: reactor, 2: condenser, 3: fine filter, 4: bio-petroleum, 5: heat exchanger, 6: diesel engine; (b) product yield vs. reactor temp yields -1: PG, 2: PL, 3: char; (c) fuel consumption vs. load 1: PG, 2: Diesel ; (d) specific fuel consumption of PG vs. load; and (e) power output vs. reactor temperature (1, electric power; 2, thermal power of diesel gen set; 3, total thermal power taking into account the heat utilised in the pyrolysis) [101].

were successful as alternative fuels for SI engine, though thermal efficiency was low at the lower heating values. They also found that heat capacity of the model gases affected the combustion performance. Thus dilution with $N_2$ produced better combustion than with $CO_2$, due to the lower heat capacity of the former. Emission of $NO_x$ also depended on gas composition. Thus under stoichiometric operation, 58% content of $CO_2$ as inert gas in PG resulted in almost zero $NO_x$ and $NO_x$ increased with $CO/H_2$ ratio. Emission of $NO_x$ was also reduced by lean burn technique or by retarding the ignition timing; both techniques together increased thermal efficiency. Greater $H_2$ content also tended to improve thermal efficiency [98].

### 5.2. Pyrolysis gas in CI engines

Aside from SI engines, PG can be used in CI engines also; this type of application uses dual fuel mode similar to biogas or syngas applications of the diesel engine whereby diesel is used as the pilot fuel. The amount of pilot diesel will vary depending on the PG composition and engine load. The composition of the PG may change with time and it is not feasible to store the gas in a cylinder for later use, so the engine should be connected directly with the reactor. Chirkov [101] presented a theoretical analysis of a 100 kVA PG-based dual-fuelled diesel engine CHP plant performance (Fig. 6). The study illustrates the PG consumption variation and also the techniques to control the PG flow based on the output load.

## 6. Approaches to improving the usability of pyrolysis liquid in IC engines

The generally troublesome experience of using PL reviewed in Section 4 means that, for internal combustion engine applications, PL needs up-grading if it is to be used to substitute fossil diesel without any major modifications to the engine. Low solids content, good homogeneity and stability and reasonably high flash point are some of the important desired properties. Water is the main component of PL and it is difficult to remove; water is usually miscible with the oligomeric lignin-derived components due to the solubilising effect of other polar hydrophilic compounds (low molecular wt acids, alcohols, hydroxyaldehydes and ketones) [102]. There are mainly two approaches to improve the quality of the PL, these are (i) by changing/controlling the operating parameters during the pyrolysis process including selection of the feedstock and addition of equipments and (ii) by modifying the physical and chemical properties of the PL after the pyrolysis process. We will now review the second approach.

### 6.1. Modifications/up-gradation techniques and up-graded properties of PL

Pyrolysis liquid up-gradation techniques discussed in the literature are concentration, hydrodeoxygenation, catalytic cracking, emulsification, esterification (blending/addition of chemicals such as alcohols), and steam reforming. These are discussed below:

(a) *Concentration*: Investigation into the addition of alcohol together with a concentration method was carried by Oasmaa et al. [103]. Using this method a homogeneous, stable and low viscosity PL fuel was produced without significantly reducing the flash point temperature [103]. The bottom phase of the PL was concentrated by evaporating 20–35 wt% of the liquid and as a result the heating value of the PL increased. The authors demonstrated this modification both in the laboratory and large scale. At laboratory scale, concentration was done by the evaporation in a rotavapor and at large scale it was done by adjusting the temperature (50 $\pm$ 4 °C) in the liquid scrubber [103]. The results illustrated that although LHV increased, viscosity increased when the water content in the PL was decreased. The addition of 10% methanol helped to reduce the viscosity level down considerably.

(b) *Hydrodeoxygenation and catalytic cracking*: De-oxygenation of PL is performed either through hydrodeoxygenation or catalytic cracking process. Hydrodeoxygenation process is performed in hydrogen-providing solvents activated by catalysts (Co–Mo, Ni–Mo) and their oxides. Alternatively, PL is loaded onto $Al_2O_3$ under pressurised conditions of hydrogen and/or CO. Oxygen from the PL is removed as $H_2O$ and $CO_2$ [14]. Hydrodeoxygenation of PL has received considerable attention [92,104–107]. Typical process temperature and pressure are between 250 and450 °C and 100 and 200 bar respectively. Hydro-processing rejects oxygen as $H_2O$ [26]:

$$C_1H_{1.33}O_{0.43} + 0.77H_2 \rightarrow CH_2 + 0.43H_2O$$

This up-gradation process converts PL to a more hydrocarbon-like product with increased stability, lower oxygen and water content, and lower viscosity. Zhang et al. [108] up-graded sawdust derived PL by using a catalytic hydro-treatment technique. The oily phase of PL was modified using sulphided Co–Mo–P in an autoclave with tetralin as the solvent. The oxygen content was reduced and the heating value was also improved. These authors also observed that crude PL was methanol-soluble and the up-graded PL was fossil fuel soluble [108].

In catalytic cracking technique, oxygen containing pyrolysis liquid is catalytically decomposed to hydrocarbons with the removal of oxygen [14]. Different types of catalysts were investigated by researchers to upgrade PL. Zeolite cracking rejects oxygen as $CO_2$ [26]:

$$C_1H_{1.33}O_{0.43} + 0.13O_2 \rightarrow 0.66CH_2 + 0.34CO_2$$

This is a close coupled process which requires constant catalyst regeneration. No hydrogen is required and the projected yield contains around 20% aromatics [26]. Yakovlev et al. [109] investigated hydrodeoxygenation of aliphatic and aromatic oxy-organics using various types of nickel-based catalysts on supports of $SiO_2$, $Al_2O_3$, $ZiO_2$, $CeO_2$ and $CeO_2$–$ZrO_2$. They observed that the Ni–Cu catalysts were more attractive than single Ni catalysts and concluded that Ni–Cu/$CeO_2$–$ZrO_2$ and Ni–Cu/$CeO_2$ combination were most effective [109]. Adjaye and Bakhshi [110,111] up-graded wood derived PL (produced using the ENSYN RTP-3 process) into hydrocarbons using a wide range of catalysts. They reported that catalysts HZSM-5, H-Y and H-mordenite (acidic zeolite catalysts) were more effective than other less acidic silica-alumina and non-acidic silicalite types [110,111]. HZSM-5 was the most effective for production of ODF, overall hydrocarbons and aromatic hydrocarbons; and use of silica-alumina catalysts produced minimum tar formation [110,111]. Hydrocarbon content ranged between 22 and 89 (% wt) of ODF obtained when HZSM-5 catalyst was used. In another study, acid composition decreased from about 14.5% to 3% and hydrocarbon (monocyclic and dicyclic) content was increased from about 0.5% to 17% when PL produced from sawdust was up-graded using HZSM-5 catalyst [112]. Fisk et al. [113] used supported platinum-based catalyst to up-grade PL and found that Pt/$Al_2O_3$ catalyst was very effective for oxygen removal. Their investigation showed that the oxygen content of the model PL

decreased from an initial value of 41.4–2.8% (wt) after up-gradation [113]. Williams and Nugranad [114] investigated the properties of rice husk PL (produced in a fluidised bed reactor) with and without using the ZSM-5 catalyst. They observed that the PL yield was reduced with the catalyst reaction compared to non-catalyst reaction, but the properties of the PL improved with the catalyst reaction [114]. The oxygen content and molecular weight of the PL were significantly reduced with the catalyst reaction. The oxygen converted largely to $H_2O$ at lower catalyst temperatures, and to CO and $CO_2$, at higher catalyst temperatures [114].

(c) *Blending and emulsification*: One approach to facilitate the use of PL in CI engines is blending with fossil diesel. Pyrolysis liquid is, however, generally immiscible with hydrocarbons and an emulsifier may be required. Researchers have investigated the properties and stability of PL emulsions using different types of emulsifiers [53,62,86,87,115]. Emulsions of PL with biodiesel [116,117] and fossil diesel [57–60] have also been investigated without using any emulsifier.

In one study, Khor et al. [53] prepared stable and homogeneous mixtures of PL (produced from empty fruit branches of oil palm tree using slow pyrolysis process) and fossil diesel using 5% (wt) diluted Hypermer B246SF (diluted with methanol) emulsifier, in five different mixing ratios of 75%, 50%, 25%, 10% and 5% (wt) PL. Emulsifier was added to the mixture by a syringe and stable emulsions were established after stirring for 6 h using a magnetic stirrer. The authors found that the properties of the 5–25% PL emulsions are almost comparable to fossil diesel [53].

Chiaramonti et al. [62] investigated the stability of wood PL and fossil diesel blends for a wide range of emulsifiers. Emulsions containing 25%, 50% and 75% of PL were prepared by adding 4% (wt.) emulsifier [62]. The test was performed at room temperature and a magnetic stirrer was used, the authors observed that – emulsions were more stable than pure PL, some emulsions were stable for up to 5 days before phase separation starts to appear; viscosity and stability increases with the increase of emulsifier content.

Jiang and Ellis [118] prepared a stable PL-biodiesel blend using octanol as an emulsifier (4% vol); and later the same authors studied the storage and thermal stability of the blend at temperatures of 60 and 80 °C [119]. They reported that acidity, water content and viscosity values of the blends were favourable for CI engine application [118]. Investigation of the thermal stability at 60 or 80 °C for up to 180 h revealed minimal changes [119].

Perez et al. [116] investigated the solubility of PLs (derived by fast pyrolysis from pine pellets and mallee) in biodiesel without using emulsifier. The biodiesel was produced from canola vegetable oil and ethyl acetate was added to enhance solubility. These authors reported an improvement in oxidation stability, but a poor solubility of fast PLs in biodiesel was observed. Pyrolysis liquid components such as carbolic acids, mono-phenols, furans and lignin derived oligomers were soluble in biodiesel; but sugar like compounds showed poor solubility. In another study, Garcia-Perez et al. [117] produced pyrolysis liquid from pine chips and pine pellets in a batch and auger slow pyrolysis reactor and blended it with biodiesel [117]. Fuel blends of biodiesel and PL require neutralisation with a weak base, such as $NaHCO_3$, to remove the organic acids. Water and low-molecular-weight compounds responsible for many of the undesirable fuel properties were poorly dissolved in biodiesel [117].

(d) *Other emerging techniques*: Hydrocracking in combination with steam reforming to produce both green gasoline and green diesel from PL has been developed for the US Department of Energy and it is projected that the technique could be operational by 2012 (Fig. 7). Hydrocracking and zeolite cracking in combination with a refinery concept may provide a sustainable solution for producing these green fuels [24,26] (Fig. 8). Neste (Finland) are producing green diesel on a trial basis from vegetable oil using the hydrotreating technique [120,121].

Other techniques to up-grade the PL are shown in Fig. 9. Syngas produced and char in the gasifier can be converted into green diesel product using the FT reactor (Fig. 9). Pyrolysis liquid can also be fermented to produce ethanol to use in the IC engine (Fig. 9). Kleinert Barth [123] investigated a liquid-to-liquid (LtL) technique in a bio-refinery concept in combination with ethanol production from lignocellulosic carbohydrates. Conversion takes place using a closed pyrolysis system in the presence of formic acid (which acts as a hydrogen source). Through this technique, oxygen depleted products are yielded. The authors found that the fuel produced by pyrolysing the lignin from ethanol production is of far better quality than crude PL [9,123]. The water content in LtL oil and PL was 5 – 10% and 37.5% (wt) respectively. The HHV of LtL oil was 35 – 44 MJ/kg, as compared to 17 MJ/kg

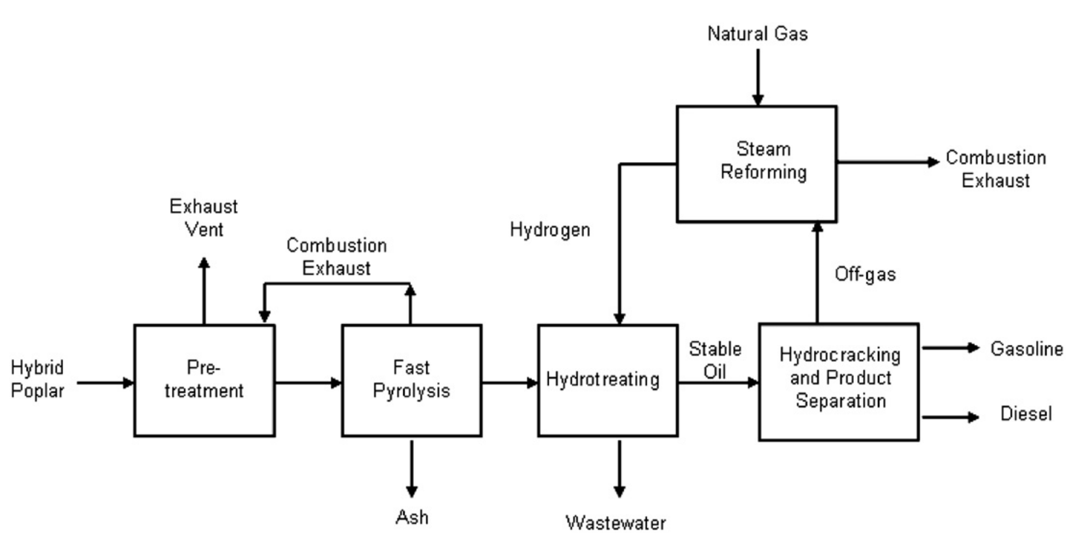



**Fig. 7.** Production of green diesel and gasoline through up-gradation of pyrolysis liquid [10].

for PL. Furthermore, LtL oil was miscible in hydrocarbons whereas PL does not [9].

Finally, we present a comparison of the up-graded PL properties vs. crude PL properties in Table 7 which shows substantial improvements in the properties of up-graded over crude PL. For example, catalytic hydro-treatment technique produced up-graded PL which has 94% higher heating value content than crude PL. The carbon content of the up-graded PL was increased by 45% and oxygen content was reduced by 93%. In another case, PL emulsion with biodiesel at 50:50 (by volume) ratio produced up-graded fuel with 98% less water content and 83.5% less acidity as compared to the crude PL. Emulsion of 30% PL with fossil diesel (made with the help of emulsifier) produced up-graded PL having a 130% higher heating value and 70% lower water content than the corresponding crude PL.

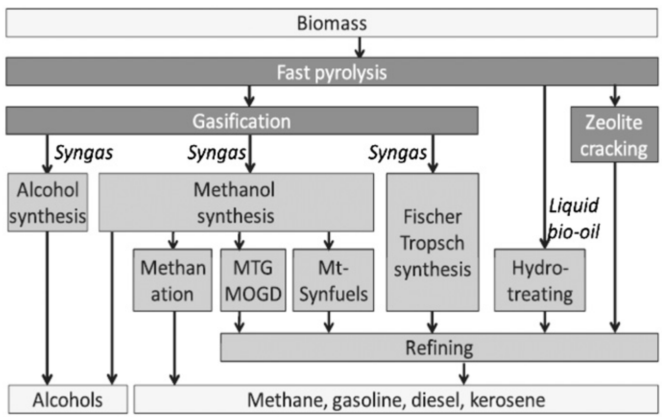



**Fig. 8.** Green diesel and gasoline products from biomass [26] (MTG – Methanol to Gasoline; MOGD – Methanol to Olefins, Gasoline and Diesel; Mt synfuel –new process via propylene).

### 6.2. *On-going major R&D activities*

Pyrolysis is a research topic of strategic interest, as evident from the numerous on-going R&D projects on processes and fuels, some of which are Bioliquids-CHP [127,128], DIABNET [129], Bio-refinery [130], BIOCOUP [20,131], EMPYRO [132,133], EBRI research [33], Pyrolysis Challenge [134], LignoValue [135]. DIBANET (Development of Integrated Biomass Approaches Network) project co-ordinated by Carbolea at the University of Limerick, Ireland aims to develop technologies by advancing the art in the production of ethyl-levulinate from organic wastes and residues. Ethyl levulinate is a novel diesel miscible biofuel. BTG-BTL is being working on 'bio-refinery' for the production of renewable fuels and chemicals from biomass, and it is expected that pyrolysis based on a 5 t/h bio-refinery plant will be demonstrated between 2015 and 2020. BIOCOUP project funded by the EU sixth framework programme, aims to develop a chain of process steps, which would allow biomass feedstock to be co-fed to a conventional oil refinery. The aim of EMPYRO project is to build and demonstrate a wood based 25 $MW_{th}$ poly-generation flash pyrolysis plant to produce electricity, process steam, pyrolysis liquid and organic acids. It was estimated that 120 t/day biomass feed would be needed to operate the plant. Recovery techniques

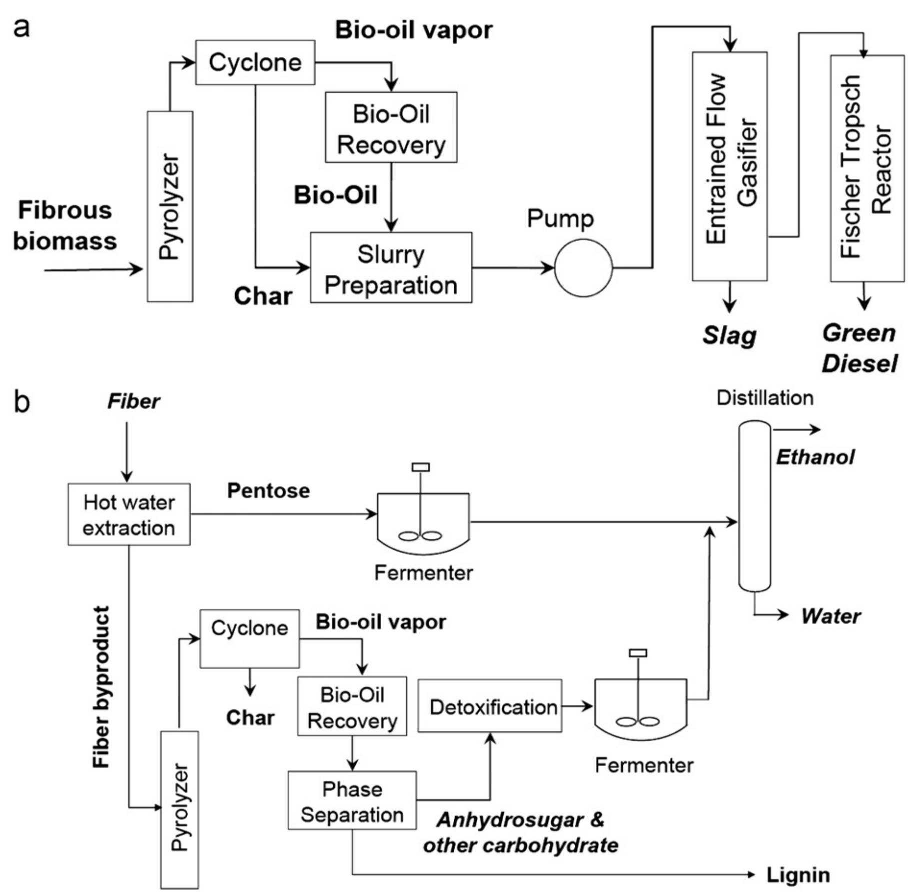



**Fig. 9.** (a) Gasification of PL for green diesel production. and (b) Fermentation of PL for ethanol production [122].

**Table 7**
Comparative properties of up-graded and crude pyrolysis liquid.

| Biomass type and pyrolysis process | Up-gradation technique | PL before and after | HHV (MJ/kg) | Viscosity (cSt) at 40 °C | Water content (% wt) | Density (kg/m$^3$) | Flash point (°C) | Acidity/ pH value | C (% wt) | H (% wt) | N (% wt) | O (% wt) | S (% wt) | Ref. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Sawdust derived fast pyrolysis liquid produced in a fluidised bed (temp. 470 °C, residence time 2 s). | Catalytic hydro-treatment of bottom phase of PL using sulphided Co-Mo-P catalyst in an autoclave with tetralin as solvent. Optimum parameters: temp. 360 °C, reaction time 30 min, and cold hydrogen pressure 2 MPa. | Before | 21.3 | — | | 1.12 | | | 60.4 | 6.9 | 0.9 | 41.8 | – | [108] |
| | | After | 41.4 | – | | 0.93 | | | 87.8 | 8.9 | 0.4 | 3.0 | – | |
| Fast pyrolysis liquid produced from beech wood. Collected from BTG, the Netherlands. | PL was catalytically hydrotreated in a 5 l batch autoclave at 320–340 °C and 200–250 bar pressure using 5% (wt) Ru/C catalyst. Mild HDO with oxygen content of 20% was further hydrotreated at 340 °C and 200 bar pressure to achieve an oxygen content of 12% (wt). (2nd stage HDO oil). | Before | 15.7 | 0.040–0.10 PaS | 27.8 | 1.2 | 40–65 | 2–3 | 39.95 | 8 | 0.04 | 52.04 | – | [91,92] |
| | | After: mild HDO | 31.8 | 0.17 PaS | 4.3 | 1.0 | 31.1 | 5 | 71.6 | 7.8 | 0.29 | 20.31 | – | |
| | | After: 2nd stage HDO | 37.5 | 0.13 PaS | 1.6 | 0.9 | 30.4 | 6 | 79 | 9 | – | 12 | – | |
| – | Catalytic cracking of PL with HZSM-5 catalyst. Atmospheric pressure, fixed bed with 15 g catalytic material inside, temp. 380 °C, feed rate 60 g/hr, 30 min. | Before | 21.22 | $2.83\times10^8$ PaS | – | 1.12 | – | – | 50.03 | 6.93 | 0.96 | 41.84 | – | [88] |
| | | After | 29.86 | $4.22\times10^7$ PaS | – | 1.03 | – | – | 71.81 | 7.18 | $<0.3$ | 21.01 | – | |
| Fast pyrolysis liquid produced from softwood residues. Soybean derived biodiesel supplied. | Emulsification of PL with biodiesel (BD) using octanol (4% vol) emulsifier. Stirring intensity: 1200 rpm, mixing time: 15 min, and emulsifying temperature: 30 °C. | Original PL | – | $67.39\times10^{-3}$ PaS at 25 °C | 28.05 | 1.2 | – | 79.23 mg of KOH/g | – | – | – | – | – | [118,119] |
| | | Original biodiesel | – | $6.590\times10^{-3}$ PaS at 25 °C; | 0.1607 | 0.881 | – | 0.55 mg of KOH/g | – | – | – | – | – | |
| | | 50% PL, 50% BD | – | $4.917\times10^{-3}$ PaS at 25 °C | 0.4634 | 0.897 | – | 13.08 mg of KOH/g | – | – | – | – | – | |
| Rice husk derived fast pyrolysis liquid. Fluidised bed reactor. | Reactive rectification using the solid acids catalysts. After reaction, light portion was separated and ethanol was added to water insoluble fraction to obtain heavy liquid. Water insoluble fraction: ethanol=1: 1.1 (wt). | Before | 14.3 | 10.5 at 30 °C | 33 | 1.16 | – | 2.82 | – | – | – | – | – | [102,124] |
| | | After: light | 21.5 | 0.46 at 30 °C | 0.52 | 0.91 | – | 7.06 | – | – | – | – | – | |
| | | After: heavy | 24.5 | 3.65 at 30 °C | 5.03 | 0.95 | – | 5.35 | – | – | – | – | – | |
| Dyna1001: PL from California pine produced by Dynamotive using bubbling fluidised bed reactor. Fast pyrolysis process. | Emulsification: 25% Dyna1001, 74% diesel fuel and 1% additive (mixture of polymeric surfactants and short chain additives). | Before | 18.16 | 0.046 PaS at 25 °C | 31.1 | 1.175 | – | 2.6 | 43.52 | 6.31 | 0.07 | 50.07 | $<0.01$ | [62] |
| | | After | 38.49 | 9.79 at 25 °C | 7.7 | 0.923 | – | 3 | 74.63 | 12.27 | 0.03 | 13.04 | $<0.01$ | |
| | 50% Dyna1001, 49% diesel fuel and 1% additive | After | 30.645 | 25.41 at 25 °C | 15.3 | 1.008 | – | 2.9 | 61.82 | 10.50 | 0.05 | 27.6 | $<0.01$ | |
| Slow pyrolysis of oil palm empty fruit branches. Heating rate: 5 °C/ min, temp: 600 °C, and reaction time: 2 h. | Hypermer B246SF was used as emulsifier. Emulsifier was first diluted with methanol at a ratio of 2:5 (v/v). Stable and homogeneous emulsions were prepared by mixing PL and 5% (wt) of diluted emulsifier. | Before | 31.44 | 13.52at 50 °C | – | 1.031 | 65 | 3.6 | 68.26 | 8.02 | 2.02 | 21.57 | 0.03 | [53] |
| | | 25% PL | 39.32 | 6.93 at 50 °C | – | 0.967 | 93 | 4.6 | 80.54 | 10.02 | 0.97 | 8.35 | 0.07 | |
| | | 75% PL | 34.23 | 10.83 at 50 °C | – | 1.028 | 73 | 3.7 | 72.23 | 9.02 | 1.87 | 16.75 | 0.05 | |
| Slow pyrolysis of palm kernel cake in a tubular fixed bed reactor. Temp: 700 °C, heating rate: 20 °C/min | Blending of organic phase of PL with fossil diesel (D), ethanol (99.8%) (ET) and n-butanol (98%) (BU). | Before | 39.50 | 58.70 | – | 1.120 | 82 | 5.87 | – | – | – | – | – | [125] |
| | | PL:10, D:50, BU:40 | 41.2 | 3.53 | – | 0.838 | 40 | 6.54 | – | – | – | – | – | |
| | | PL:30, D:10, BU:60 | 37.2 | 5.86 | – | 0.891 | 41 | 6.24 | – | – | – | – | – | |
| Rice husk derived fast PL. Temp: 475 °C. PL filtered in centrifuge to remove big particles. | Emulsion with fossil diesel. Two emulsions were produced using 1.5% (wt) emulsifier in both cases. | Before | 15.4 | 10.2 | 32.3 | 1.13 | – | 3.2 | 37.48 | 8.28 | 0.59 | 53.45 | 0.036 | [126] |
| | | 10% PL | 41.9 | 4.9 | 3.3 | 0.88 | – | 3.4 | – | – | – | – | – | |
| | | 30% PL | 35.5 | 8.0 | 9.7 | 0.93 | – | 3.3 | – | – | – | – | – | |

of acetic acid from the aqueous organic acid solution of PL will be developed. The European Biofuel Research Institute (EBRI) in Aston University (UK) is working on the combined intermediate pyrolysis-gasification concept for co-generation applications. It is proposed to use the set up as the basis for a combined heat and power system for the University campus. Pyrolysis Challenge, funded by Carbon Trust (UK), aims to demonstrate 'proof of scientific and engineering principles for a novel process for the production of a low-cost and low GHG intensity up-graded pyrolysis liquid'.

## 7. Storage stability, and corrosion and spray characteristics of pyrolysis liquid

### 7.1. Storage stability and ageing

Pyrolysis liquid is normally unstable; re-polymerisation occurs with time and hence viscosity increases [136–138]. Lighter compounds present in the PL cause this ageing process. During ageing PL tends to separate into various tarry, sludgy, waxy, and thin aqueous phases [139]. The volatility of PL decreases with time.

System studies of storage stability have been carried out [137,138]. Czernik et al. [137] studied wood-derived fast PL at three different temperatures (37, 60 and 90 °C). Using GPC (molecular weight distribution) and FTIR spectroscopy, they found that the pH value remained un-changed; but the viscosity, water content and molecular weight values increased with ageing [137]. These authors also observed that:

- viscosity increased considerably quicker at 60 and 90 °C than at 37 °C: for example, at 37 °C viscosity increased by about 70% in 84 days; whereas at 90 °C, the viscosity was increased by around 2.15 times just only after 15 h of ageing.
- changes in the water content due to ageing at low temperature were not significant, but the change was noticeable when the PL was kept at high temperature. Water content was increased by ~3% after 84 days of ageing at 37 °C; and the same was increased by about 8.6% after 9 days when PL was aged 60 °C.
- molecular weight increased when the PL was stored, due to the polymerisation. The rate of increase was higher at elevated temperature. Thus molecular weight increased by about 70% after 9 days at 60 °C, compared to 40% after 84 days at 37 °C.

However, the addition of some inhibitors (e.g. hydroquinone) helps to reduce the rate of increase in the viscosity of PL by suppressing the thermal polymerisation reactions [53]. For highly viscous PL, preheating to reduce the viscosity before injection may lead to chemical changes of the PL. Ageing of PL can cause problems in CI engines, so use of fresh PL instead of using aged PL is recommended. Hot fuel bled from the injectors should be by-passed to avoid polymerisation in the fuel supply loop. The bled fuel can be reused after up-grading.

### 7.2. Corrosion and spray characteristics

Frigo et al. [72] tested the corrosion properties of wood PL produced using flash pyrolysis. They immersed steel plates with high surface to volume ratio in PL baths at different temperatures and durations. The resulting metal losses after 2 h 34% and 43.5% at 50 °C and 90 °C respectively; and 90% was lost after 24 h at 90 °C.

Corrosion tests were also carried out by Qiang et al. [126] using both crude and up-graded PL with fossil diesel. The crude PL was centrifuged to eliminate large solid particles and, using an ultrasonic emulsifier; two emulsions were prepared with 88.5% and 68.5% PL (wt). The emulsions were stable for up to 10 days [126]. The samples were tested with four different metals: aluminium, mild steel (Q235A), brass (H62) and austenite stainless steel (SS321, 1Cr18Ni9Ti). The results showed that aluminium and mild steel have poor resistance to crude PL and its emulsions; brass is also affected by them. Stainless steel, however, was corrosion-resistant against both crude PL and its emulsions, because a $Cr_2O_3$ film formed on its surface prevented the underlying iron from being corroded [126].

Corrosion tests of PL with standard injector components were also conducted at VTT, Finland. Jay et al. [79] measured the dimensional changes of injector components after soaking in wood PL for 7 weeks. They observed severe corrosion [79]. Later VTT and Wärtsilä jointly worked on the material development of the injector components and recommended the stainless steel alloys and polymers shown in Table 8. Though based on studies with wood derived PL, Table 8 serves as a guideline for PL from other types of biomass.

Analysis of the spray characteristics of PL is important to assess the combustion behaviour in engines. The importance of viscosity, density and surface tension in affecting the spray pattern during the injection system can be quantified in terms of the SMD of droplets, given by

$$SMD = 3.08 \nu^{0.335} \sigma \rho_L^{0.737} \rho_A^{0.06} \Delta P^{-0.54}$$

where $\nu$ is the kinematic viscosity in $m^2/s$; $\sigma$ is the surface tension in N/m; $\rho_L$ is the density of the fuel and $\rho_A$ that of the ambient air in $kg/m^3$; and $\Delta P$ is the nozzle opening pressure in Pa [140]. Higher viscosity of fuels leads to larger droplets. In addition, droplet size also depend on the nozzle hole diameter. Frigo et al. [72] developed an injector test rig, where a single hole injector was used to inject PL and fossil diesel in quiescent air at atmospheric pressure. The SMD and droplet size distribution were analysed at different temperatures. The SMD of wood flash pyrolysis liquid was much higher than for fossil diesel, although

**Table 8**
Materials selection for injection components for wood PL operation [79].

| Components | Required properties | Selected properties/materials |
|---|---|---|
| Nozzle body | Corrosion resistance, ability to withstand high temp. ~260 °C, strength 1200 N/mm$^2$. hardness >61 HRc | Martensitic stainless steel (M390) with a composition of C 1.90%, Cr 20%, Mo 1%, V 4% and 0.6% W; which can be through hardened to achieve a 62 HRc and can withstand up to 500 °C. |
| Injector holders and bodies | – | X35CrMo17. A martensitic steel with a UTS value 750–900 N/mm$^2$ and 49 RHc. |
| Pushrods and needles | – | X90CrMoV18 (AISI 440B) stoff 1.4112 martensitic stainless steel, 57 HRc. |
| Springs | – | Stoff 1.4310 austenitic stainless steels 600–900 N/mm$^2$ UTS. |
| Sealing | – | EPDM and teflon O rings. Viton O rings react with wood PL which causes material expansion. Copper is suitable as washers. |

it decreased with temperature. Droplet size distribution also improved with the increase of temperature.

## 8. Engine durability, and environment and economics

### 8.1. Engine durability issues

The findings regarding engine performance and exhaust emissions presented in Table 4a and b are based on short-term engine tests lasting from minutes to hours. Long-term engine testing with modified PL in standard and modified engines is needed but so far few results are published. Various engine durability problems could occur even with modified PL use e.g. (i) coking of the fuel pump and injector system and wear of the injectors, (ii) carbon deposits inside the cylinder, (iii) piston ring sticking and valve jamming, (iv) wear due to corrosiveness of PL, (v) clogging of fuel filters and the fuel supply line, (vi) wearing of the seals/ gaskets, and (vii) lubricating oil contamination due to entry of un-burnt PL into the crankcase.

Wear is one of the main parameters monitored during long-term engine testing. The most vulnerable parts are the piston, piston ring, cylinder, crankshaft, valves, camshaft and lubricating oil pumps. Loss of pressure or viscosity in the lubricating oil aggravates wear. On the other hand, formation of resinous products due to lubricating oil oxidation, evaporation of lighter fractions, anti-wear additives, and the presence of insoluble contaminants tends to increase the viscosity [141]. Intrusion of PL into the crankcase can result in thickening or gelling of the lubricant and may make the lubricating oil more corrosive. Lubricating oil change is recommended if the viscosity increases by $>20\%$, or decreases by $>10\%$ [141].

### 8.2. Environmental and economical issues

Hoefnagels et al. [142] investigated the life cycles of different biofuel production systems and found a wide range of variation in GHG emission performance (even for the same biofuel type) depending on location of crop cultivation (and related yields and soil $N_2O$ emission), allocation procedure for co-products and choice of reference system. Well-to-wheels GHG emissions of a number of biofuels show that PL can help to reduce emissions by around 60% (Table 9). However, the reductions are not as great as for some biofuels which can reportedly achieve GHG savings of over 100% compared to fossil fuels, as the biomass provides both the feedstock and much of the process energy for its own conversion [142].

Though PL is costly at the moment it is still at the development stage [17,143]. Bridgwater [17] estimated that, per unit energy, PL costs 10–100% more than fossil fuel. Electricity costs have been estimated at 0.091–0.199 euro/kW h for electricity generated by fast pyrolysis in CI engine and 0.024–0.119 euro/kW h for integrated pyrolysis combined cycle (IPCC) electricity generation plant [37,144]. The IPCC system is advantageous at higher biomass price [144]. Wright et al. [145] illustrated that transportation grade fuel such as naphtha and diesel could be produced through fast pyrolysis of corn stover and subsequent up-grading at a competitive cost of US$ 0.56–0.82 per litre. However, the cost of production was higher at US$ 1.73/litre based on the construction of a pioneer (i.e. first of its kind) plant [145].

## 9. Discussion and conclusions

The quality and yield of PL and PG are dependent on many variables such as operating parameters (e.g. temperature, residence time), biomass feed types and composition, and the pyrolysis techniques used, including the reactor type and accessories. Pyrolysis of biomass with high lignin content produces PL of high calorific value.

The physical and chemical properties of PL are very different to fossil diesel. Pyrolysis liquid is highly acidic (pH: 2–4), its heating value is little more than half that of fossil diesel, and its density is around 30–40% higher. The water content (15–30% wt.) in PL is difficult to eliminate by drying. Compared to fossil diesel, the viscosity of PL is much higher, its typical molecular mass is almost double and the SMD of PL is almost 20% higher. Pyrolysis liquid is unstable and difficult to store, as properties such as viscosity, molecular mass and chemical composition change with temperature and time. The carbon content is only 40–60% (wt) for fast PL and about 70–80% for slow PL, compared to 87% for fossil diesel. The oxygen content is high, typically 35–50% (wt) for fast PL, though somewhat lower at around 10% (wt) for slow PL. Fast PL is immiscible with fossil fuels due to high oxygen content in the PL; however, PL produced through slow pyrolysis process is more miscible due to lower oxygen content. Inert gas (mainly nitrogen) constitutes around 80–90% (wt) of PG alongside mixtures of CO, $CH_4$, $CO_2$ and $C_2H_n$ gases. Pyrolysis gas has low calorific value (5.5–7.0 MJ/$m^3$) compared to around 37 MJ/$m^3$ for natural gas.

**Table 9**
GHG emissions reduction scenarios of some advanced biofuels [143].

| Fossil/biofuels | Feedstock | Process | Well-to-wheels GHG emissions | |
|---|---|---|---|---|
| | | | $CO_2$-equivalent emissions (g/km) | % reduction vs. fossil gasoline/diesel |
| Diesel | Fossil/petroleum | Refining | 198 | – |
| Biodiesel | Rapeseed | Oil to FAME (transesterification) | 123 | 38 |
| Biodiesel | Soybeans | Oil to FAME (transesterification) | 94 | 53 |
| Diesel | Biomass – eucalyptus (Baltic) | HTU Biocrude | 79 | 60 |
| Diesel | Biomass – eucalyptus (Baltic) | Gasification/ F-T | −16 | 108 |
| Diesel | Biomass – eucalyptus (Baltic) | Pyrolysis | 72 | 64 |
| DME | Biomass – eucalyptus (Baltic) | Gasification/DME conversion | 22 | 89 |
| Gasoline | Fossil/petroleum | Refining | 231 | – |
| Gasoline | Biomass – eucalyptus (Baltic) | Gasification/ F-T | −10 | 104 |
| Ethanol | Biomass – poplar (Baltic) | Enzymatic hydrolysis (CBP)[a] | −28 | 112 |
| Ethanol | Biomass – poplar (Brazil) | Enzymatic hydrolysis (CBP) | −28 | 112 |
| Ethanol | Biomass – poplar (Brazil) | Enzymatic hydrolysis (CBP) | −3 | 101 |
| Ethanol | Corn | Fermentation | 65 | 72 |
| Hydrogen | Biomass – eucalyptus (Baltic) | Gasification | 11 | 95 |
| CNG | Biomass – eucalyptus | Gasification | 39 | 83 |

[a] CBP – combined bio-processing.

After reviewing almost 24 established experiments on the use of PL (both crude and up-graded) in CI engines, we have found that only about a quarter reported successful stable engine operation. Major problems associated with the combustion of the crude PL in CI engines are: poor ignition quality, corrosion and erosion of the engine components, coking of the piston and cylinder liners and subsequently seizing of the engine, and chemical instability of the PL. Though engines may be operated successfully on up-graded PL, the results generally show high fuel consumption (due to the low heating value of the PL), long ignition delay and injection duration, high CO emission, and low thermal efficiency. Low $NO_x$ emission may occur due to the high water content of PL compared to diesel; however, higher $NO_x$ emission sometimes occurs associated with the high density of PL. Inlet air preheating and addition of ignition improver help to improve the combustion behaviour of PL. Combustion of PL in CI engines is slow to start but then proceeds quickly. The long ID causes rapid in-cylinder pressure rise, which ultimately may create knocking.

Some of the more successful approaches have used slow PL blended with diesel, which has achieved stable operation with full engine power. Dual injection mode, with various types of PL and pilot injection of diesel, has also given good results; however, this involves expensive modifications to the engine.

Other fuel supply/engine modification techniques to adapt CI engines for PL are (i) increased compression ratio; (ii) no mixing of the injector return with the fresh PL supply to avoid re-polymerisation; (iii) use of corrosion resistant materials in the fuel system; and (iv) operating sequences using diesel start and stop and ethanol flushing.

Engine selection is also important. As PL is generally a low-grade fuel, low or medium speed engines tend to be more suitable than high speed engines. They are more able to withstand high mechanical and thermal stresses which are expected in the case of PL. In addition, CI engines with indirect injection systems and mechanical type injectors are preferable. Pyrolysis gas can be used either in SI engine as single fuel or in CI engines in dual fuel mode. In SI engines, emissions and performance are comparable to NG operation (except $NO_x$ gas emission). However, engine operation with PG is less stable.

To improve the properties of PL, researchers are working on various up-gradation techniques. Successful techniques include: catalytic cracking, hydrodeoxygenation and blending/emulsifying with fossil diesel (or other fuel) with or without using emulsifier. Use of up-graded PL in CI engines has resulted in successful stable engine operation and in some cases corrosion of the injectors was avoided. Sometimes, however, the use of emulsified PL led to unstable engine operation. More long term engine operation is necessary to assess the viability of using up-graded PL. Currently, many researchers are focussing on activities in hydrocracking and bio-refinery techniques to up-grade PL and thus ultimately produce green diesel and green gasoline for both stationary and mobile applications.

Interestingly, $NO_x$ emissions are lower in the case of PL and higher in the case of PG, in CI and SI engines respectively (in comparison to standard fossil diesel and NG operation). However, no results are available on soot or particulate matter emission from pyrolysis fuels in IC engines. $NO_x$ is a strong GHG and soot emission is very harmful for human health. There is a three-way trade off between $NO_x$ emission, thermal efficiency and soot emission. Overall optimisation can be achieved through techniques such as: lean burn, exhaust gas recirculation and retarding the injection/ignition timing. Some further techniques under investigation to reduce the soot emission from CI engines include: split injection (multiple injections), methanol addition and catalytic processing [146–148].

Compared to fossil diesel, PL remains expensive but commercialisation of pyrolysis technology would help to reduce the cost considerably. The cost of electricity generation based on fast pyrolysis and CI engines ($0.091-0.199$ euro/kW h) is already comparable to some other biofuel-based electricity generation such as combustion and gasification.

Areas of R&D important for successful use of pyrolysis fuels in IC engines include: (i) pyrolysis reactor design and process optimisation for specific feedstocks; (ii) in particular, slow pyrolysis of appropriate biomass and direct blending of the slow PL with fossil diesel; (iii) PL-biodiesel blending (and PL-biodiesel-alcohol blending), characterisation of these blends and testing in CI engines; (iv) investigation of biomass feedstock species that may yield fossil diesel-miscible PL; (v) filtration/centrifugation techniques to reduce the solids content in PL; (vi) further investigation into the effect of varying air intake pressure and temperature, injection pressure, injection timing and ignition delay; (vii) development of injectors (including angle of injection and number of holes), fuel pumps and fuel supply systems; (viii) investigation into $NO_x$ and soot emissions and ways to reduce them; (ix) dual injection systems including piston/combustion geometry; (x) development of inexpensive additives/emulsifiers to prepare diesel (or other fuel) miscible blends; (xi) esterification by adding solvents to reduce polymerisation in storage; (xii) antioxidants to reduce olefin polymerisation reactions; (xiii) investigation of the catalysts and steady use in the reactors for up-gradation of PL including the economics of such activities; (xiv) investigation into additives/emulsifiers to increase the flash point of the PL; and (xv) long term operation and scale up of reactors to ensure the availability of PL.

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